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OXIDATION OF SODIUM SULPHIDE AND HYDROSULPHIDE TO THE SULPHATE BY ELECTROLYSIS.

BY FRANK W. DURKEE.

It is very well known that potassium and sodium chlorates can be made from the chlorides in solution by electrolysis, and various other substances oxidized by the same means. Sodium sulphate mixed with acid sodium hydrosulphite, $NaHS_2O_4$, has been produced from acid sodium sulphite,[1] but I am not aware that any one before has attempted to make sulphates from the alkaline sulphides and hydrosulphides by electrolysis. At the request of Mr. F. S. Pearson, Engineer of the Metropolitan Traction Co., of New York City, experiments were begun to show whether or not it would be possible to transform the ammonium compounds in gas liquors directly into sulphate of ammonium by use of the electric current. In the preliminary experiments, gas carbon electrodes were used, and ammoniacal sulphide and hydrosulphide solutions, but with this arrangement the three-ampere current, which passed through the solution for several hours, failed to produce any sulphate. The sulphide solution was blackened, however, by the finely divided particles of carbon which separated from the electrodes. Copper electrodes,

[1] E. H. Ekker: Rec. Trav. Chim., 14, 57–64, (1895).

when used in place of the carbon, were soon covered with copper sulphide and the ammonium sulphur compounds were not oxidized. The oxidation went on very well when platinum electrodes were used, and ammonium sulphate in considerable quantity was produced. Solutions of sodium hydrosulphide and sodium sulphide were then subjected to electrolysis, and sulphate of sodium obtained. These experiments, however, were not conducted in a way to show that all of the alkaline metals in the compounds present could be changed to sulphate by electrolysis. This point seemed of so much importance that an attempt was made to settle it, first of all, at the beginning of the investigation and in the following way :

Fifty cc. of a solution of sodium hydroxide, prepared from sodium and distilled water, were measured out into a small flask, and supersaturated with hydrogen sulphide. An equal volume of the same solution of sodium hydroxide was then added, and the resulting solution, approximating a sulphide, was poured into a tall beaker of about one liter capacity. 300 cc. of water were added. To prevent loss by spattering during the process of electrolysis, the beaker was covered with a watch-glass, notched to admit the wires which extended to the electrodes. The electrodes themselves, of thick platinum foil, were cylindrical in form, three inches long and one inch in diameter. Heavy platinum wires connected the electrodes to the battery circuit. When in use, the electrodes were thrust nearly to the bottom of the beaker, were parallel, and one and a half inches apart. After proper connections had been made with a storage battery, a current of about 3.1 amperes flowed through the liquid for about eleven hours and thirty-five minutes. Then the circuit was broken and the solid matter, mostly sulphur, filtered out. Afterwards enough water was added to the filtrate to make 1000 cc. A second solution was then prepared in exactly the same way as the first and made up to 1000 cc.

It followed, therefore, that 1 cc. of the new solution contained as much sodium as 0.1 cc. of the original solution of sodium hydroxide, and 25 cc. as much as 2.5 cc. of the solution of hydroxide. If, then, pains be taken to determine ac-

curately the weight of sodium combined as sulphate in 25 cc. of the solution after electrolysis, it should exactly equal the weight of the sodium in 2.5 cc. of the solution of hydroxide, if the oxidation to sulphate by electrolysis is complete and quantitative. Tested qualitatively, the solutions were neutral and gave the reactions only of sodium sulphate. Consequently, to get the weight of sodium sulphate, it is only necessary to evaporate to dryness in a weighed platinum crucible, on a water-bath, 25 cc. of the solutions after electrolysis, heat and weigh. The weight of the sodium could then be calculated from the weight of sodium sulphate found. Duplicate determinations of sodium sulphate were made in each solution and the results are below.

Solution No. I.

a. Weight of Na_2SO_4 in 25 cc., 0.2641 gram.

b. Weight of Na_2SO_4 in 25 cc., 0.2653 gram.

Weight of Na calculated from an average of weights of Na_2SO_4 obtained in the above determination 0.0857 gram.

Solution No. II.

a. Weight of Na_2SO_4 in 25 cc., 0.2636 gram.

b. Weight of Na_2SO_4 in 25 cc., 0.2638 gram.

Weight of Na calculated from an average of the weights of Na_2SO_4 obtained in the above determinations 0.0854 gram.

To determine the effects of the electric current upon solutions of hydrosulphide of sodium, 100 cc. of the solution of sodium hydroxide were supersaturated with hydrogen sulphide, diluted to 400 cc. by addition of water, and treated for about eleven hours with a three-ampere current. Considerable sulphur separated. This was filtered off and enough water added to make 1000 cc. During the electrolysis some of the sulphur was oxidized to sulphuric acid, as was shown, both by the use of blue litmus paper and by a quantitative determination with barium chloride in hydrochloric acid solution. In all, two solutions, like the one just described, were prepared and analyzed as before, with the following results:

Solution No. I.

a. Weight of Na_2SO_4 in 25 cc., 0.2648 gram.

b. Weight of Na_2SO_4 in 25 cc., 0.2638 gram.

Weight of sodium calculated from an average of the weights Na_2SO_4 obtained in the above determinations 0.08545 gram.

Solution No. II.

a. Weight of Na_2SO_4 in 25 cc., 0.2636 gram.

b. Weight of Na_2SO_4 in 25 cc., 0.2640 gram.

Weight of sodium calculated from an average of the weights of Na_2SO_4 obtained in the above determinations 0.08545 gram.

Determined by standard acid, the sodium in 2.5 cc. solution of sodium hydroxide was 0.0860 gram. The sulphate method gave, as an average of duplicate determinations, 0.0858 gram, and the average of 0.0860 gram and 0.0858 gram is 0.0859 gram, the weight of sodium in 2.5 cc. of the solution of sodium hydroxide.

This weight, 0.0859 gram, should correspond to the weight of sodium in 25 cc. of the solution after electrolysis, if the oxidation of the sulphur compounds to sulphate is complete. For the sake of a better opportunity for comparison, the figures already obtained by analysis have been inserted below in a group.

Sodium in 2.5 cc. NaOH solution, 0.0859 gram.

Solution of Na_2S after Electrolysis.

Sodium in 25 cc. of No. I,	0.0857 gram.
Sodium in 25 cc. of No. II,	0.0854 gram.

Solution of NaSH after Electrolysis.

Sodium in 22 cc. of No. I,	0.08545 gram.
Sodium in 25 cc. of No. II,	0.08545 gram.

While the weights of sodium found in 25 cc. of the solutions after electrolysis do not exactly agree with the weight found in 2.5 cc. of the solution of sodium hydroxide, the agreement is so close that the complete change of sulphide and hydrosulphide to sulphate by electrolysis seems certain.

By what chemical change or changes is sulphate of sodium produced from sodium sulphide electrolytically? During the

electrolysis of sulphide solutions, in the apparatus before described, some information on this point has been obtained by inspection. As soon as the current began its work electrolytic hydrogen escaped rapidly from the solution about the negative electrode. On the other hand, very little oxygen escaped at the positive. After the current had passed for a short time, the solutions, nearly colorless at first, grew yellow about the negative electrode, and the yellow color rapidly diffused throughout the electrolyte. Later light yellow sulphur made its appearance on the positive electrode. It scaled off, however, as the electrolytic process proceeded, and the greater part dissolved in the surrounding liquid. Next, in order, fine, white sulphur separated in little clouds about the positive electrode, near the surface of the liquid, but dissolved completely as it sank toward the bottom of the beaker cell. With the continuation of the electrolytic process, the clouds of fine, white sulphur became larger and denser, so that immediately before the yellow color disappeared from the electrolyte altogether, they did not dissolve, but gradually diffused throughout the liquid and finally settled down upon the bottom of the beaker. At this stage of the electrolysis, and a little later, much more oxygen escaped from the solution than at any previous time during the passage of the electric current. The solutions were gradually warmed by the electrolytic action.

Taken up in reverse order, the phenomena above described are to be interpreted as follows: The fine white sulphur separating in little clouds about the positive electrode, shows that sodium thiosulphate, $Na_2S_2O_3$, is present and being oxidized to sulphate in the electrolyte, while the light yellow sulphur, which adheres at first to the positive electrode, indicates the presence of polysulphides. These assertions rest upon the data collected during the electrolysis of sodium polysulphide and thiosulphate solutions in the apparatus already described. By such experiments, it has been found, that the sulphur from a thiosulphate solution always comes down finely divided and white, and does not adhere closely to the positive electrode. In a polysulphide solution, on the other hand, it clings tightly to the positive electrode at first,

later scales off, and is light yellow in color. The yellow color of the electrolyte also indicates the presence of polysulphides. Again after filtering off the precipitate formed by adding excess of ammoniacal zinc solution, the filtrate always gives the reactions of thiosulphate, on addition of an acid, provided the electrolysis is broken off after the little clouds of white sulphur begin to separate. The oxidation of sodium sulphide and hydrosulphide to sulphate is complete when the white sulphur separates no longer at the positive electrode. As for the electrolytic hydrogen, since it escapes from the electrolyte, it could not have acted chemically upon any substance therein. Moreover, if it had acted chemically, it must have acted as a reducing agent, in which event, from the nature of the substances in the liquid, sulphur would probably have separated at the negative electrode instead of the positive, just as it does in the electrolysis of aqueous solutions of sulphur dioxide, or would have combined with the liberated hydrogen to form hydrogen sulphide. But nothing of the sort happens. On the other hand, since electrolytic oxygen does not escape from the electrolyte, at least not during the first stages of the electrolysis, it must combine chemically to oxidize some substance or substances in the solution. It would seem very probable, therefore, that the oxidation of sodium sulphide and hydrosulphide to the sulphate is not retarded to any extent, at least, by the presence of electrolytic hydrogen, in which event the oxidation might be expected to go on, except so far as rate is concerned, is very much the same way that it does when air is drawn through solutions of sodium sulphide.

Drawing air through solutions of sodium sulphide, according to Lunge,[1] first produces sodium hydroxide and sodium thiosulphate: $2Na_2S + 4O + H_2O = 2NaOH + Na_2S_2O_3$. The thiosulphate then takes oxygen from the air and forms sodium sulphate, and sulphur separates: $Na_2S_2O_3 + O = Na_2SO_4 + S$. Afterwards yellow polysulphides result from the solution of the free sulphur in sodium sulphide and hydroxide, come in contact with more oxygen, sulphur separates again, and an additional amount of thiosulphate is pro-

[1] Soda Industry, p. 531.

duced: $Na_2S_4 + 3O = Na_2S_2O_3 + 3S$.[1] Very likely other polysulphides are produced, but are all changed to the thiosulphate by the free oxygen, according to similar reactions.

If, therefore, the electrolytic oxidation of sodium sulphide to the sulphate takes place as above described, at any instance after the electric current has acted on the solution for some time, and indeed, until very near the end of the electrolytic oxidation, the sum of the weights of sodium in the sulphide, hydroxide, sulphate, thiosulphate, and polysulphide, must equal the weight of sodium in the solution of sodium sulphide before electrolysis. Moreover, if these weights do equal each other, it follows that the oxidation takes place through the formation of these compounds and no others. So, to settle the point under consideration, it is only necessary to subject solutions of sodium sulphide to electrolytic action for different periods of time, and then to rigorous quantitative analysis, in order to determine whether the oxidation takes place according to the above reactions or not.

For convenience, the sulphide solutions, intended for analysis and described below, have been numbered.

Number I. was prepared by supersaturating with hydrogen sulphide 50 cc. of the solution of sodium hydroxide, already described and analyzed, and adding 50 cc. more of the same solution of sodium hydroxide. After diluting with 300 cc. of water, the solution was subjected to electrolysis, in the apparatus before used. A 3.1 ampere current passed for one hour and thirty minutes, after which the solution was filtered and made up to 1000 cc. by addition of water. Numbers II., III., IV. and V. were prepared by the method used in the preparation of No. I., but the electric current and time of electrolysis varied in each case. No. II. was subjected to the action of a 3.1 ampere current for two hours; No. III. to a 3.2 ampere current for two hours and thirty minutes; No. IV. to a 3.0 ampere current for two hours and thirty minutes; No V. to a 3.1 ampere current for six hours and forty minutes. As a high reading ampere meter was used a part of the time, in some cases, the above figures representing amperes, may not be entirely reliable.

[1] Dopping: Ann. Chem. (Liebig), **46**, 172.

In 50 cc. of the electrolytes, which, theoretically, contain as much sodium as 5 cc. of the solution of sodium hydroxide, the determination of sodium in the different compounds has been made by the following analytical methods: To get the weight of sodium in the sulphate, hydrochloric acid and barium chloride have been added to 50 cc. of the electrolytes, and the resulting barium sulphate determined in the usual way. The weight of sodium in sodium sulphate has then been calculated from the weight of barium sulphate obtained.

The weight of sodium in sulphides has been obtained by use of standard zinc solution, prepared by dissolving 3.253 grams of pure zinc in hydrochloric acid and adding ammonia to supersaturate the liquid. Enough water was then added to make 1000 cc. Nickel nitrate upon a white plate has been used as indicator in these titrations.

The first step in the method used for the determination of sodium in the form of the thiosulphate has been to add to the solution a slight excess of the zinc solution described above. The resulting sulphide of zinc and free sulphur have then been filtered off, excluding the air as much as possible meanwhile, and excess of bromine has been added to the filtrate to oxidize the thiosulphate to acid sulphate. After acidifying with hydrochloric acid, an excess of barium chloride has been added, the weight of the barium sulphate afterward determined in the usual way, and from it the corresponding weight of sodium calculated. By subtracting from this the weight of sodium found in sodium sulphate, twice the weight of the sodium combined in the thiosulphate has been obtained.

In the determination of sodium in the form of hydroxide, a large excess of standard sulphuric acid has been added to 50 cc. of the electrolyte solutions. Afterwards they have been rapidly boiled to expel sulphur dioxide and hydrogen sulphide, filtered and titrated back with standard sodium hydroxide, using methyl orange in cold solution as indicator. By subtracting the weight of the sodium in the standard solution of sodium hydroxide used, from the weight of sodium that the standard sulphuric acid would neutralize, the weight of sodium acted upon by the standard sulphuric acid in the

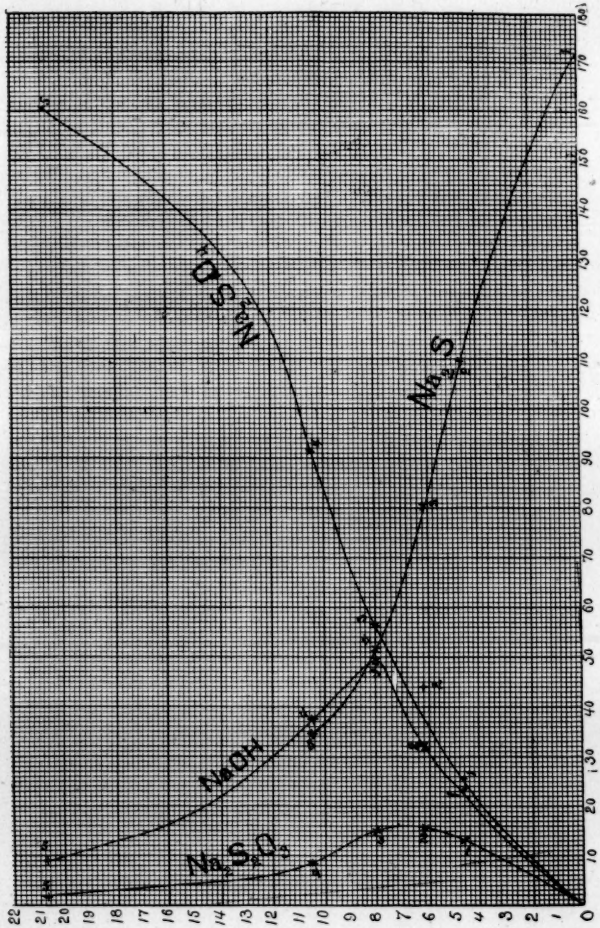
electrolyte solution under examination has been obtained. The difference between this weight of sodium and the sum of the weights of sodium in sulphides and thiosulphate equals the weight of sodium in the hydroxide.

For the sake of comparison, the analytical results have been arranged in tabular form. The results themselves are averages obtained in duplicate determinations. The weights are given in grams:

Solutions.	No. I.	No. II.	No. III.	No. IV.	No. V.
Time,	1 h. 30 m.	2 h.	2 h. 30 m.	3 h. 30 m.	6 h. 40 m.
Amperes,	3.1	3.1	3.2	3	3.1
Ampere-hours,	4.6	6.2	8	10.5	20.7
Na in Na_2SO_4,	0.0251	0.0441	0.0563	0.0915	0.1604
Na in Na_2S,	0.1096	0.0806	0.0515	0.0354	....
Na in $Na_2S_2O_3$,	0.0131	0.0158	0.0145	0.0086	0.0019
Na in NaOH,	0.0236	0.0320	0.0492	0.0367	0.0090
	0.1714	0.1725	0.1715	0.1722	0.1713

Barring experimental errors in the preparation of the standard solution subjected to electrolysis and analysis, each should contain 0.1718 gram of sodium per 50 cc. It will be seen that the weight of sodium in sodium thiosulphate plus sodium in the hydroxide, sulphate and sulphides corresponds so closely to the theoretical weight of sodium in 50 cc. of the solution that it seems impossible to have the oxidation take place through the formation of any compound or compounds of sodium besides those above mentioned. Sulphides disappear first, the hydroxide next, and the thiosulphate last of all. By using ampere-hours and milligrams of sodium in the sulphide, thiosulphate, sulphate and hydroxide, the oxidation curves below have been plotted. One square to the right of the zero mark represents 1 mg. of sodium, while five squares upward represent an ampere-hour.

The method used for the estimation of the polysulphides of sodium is based upon the fact that, when an alkaline solution of zinc chloride is added to a solution of polysulphides, the sulphur above one atom separates out, and zinc sulphide is produced. The free and combined sulphur can then be filtered off, oxidized to sulphuric acid and zinc sulphate by


$Na_2S_2O_3$
NaOH
Na_2S
$Na_2S_4O_6$
22 21 20 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180

bromine, and calculated from the weight of the barium sulphate which results on addition of hydrochloric acid and barium chloride. The resulting weight of sulphur is that of all the sulphur in sulphides and polysulphides. By subtracting the weight of sulphur that would combine with the weight of sodium, found by means of the standard solution of zinc chloride, to form sodium sulphide, the weight of sulphur in the polysulphides of sodium above one atom has been obtained.

Solutions I., II., III. and IV. gave the following weights (in grams) of sulphur above one atom in the polysulphides:

I.	II.	III.	IV.
0.0208	0.0256	0.0415	0.0199

These determinations are valuable inasmuch as they show the amount of polysulphide present at different stages of the electrolysis and correspond, as nearly as could be judged, to the varying intensity of the yellow color in the solutions.

The effect of a three ampere current at 50 volts, alternating 130 times per second, was next tried upon three sulphide solutions.

Platinum wire, either double or single, was used for the electrodes. After the electrolysis, the solutions were filtered and diluted with water to 1000 cc. Theoretically, therefore, 50 cc. of No. I. contain 0.1716 gram of sodium; No. II., 0.1802 gram; and No. III., 0.1802 gram. The methods used in the analyses of the solutions obtained by use of the direct current and already described have been used over again in the analyses of I., II. and III., and the results are below. The weights are given in grams.

Solutions.	No. I.	No. II.	No. III.
Approximate time of electrolysis,	2 h.	3 h. 30 m.	5 h.
Approximate number of amperes,	3	3	3
Na in Na_2SO_4,	0.0033	0.0107	0.0218
Na in Na_2S,	0.1596	0.1152	0.0857
Na in $Na_2S_2O_3$,	0.0022	0.0249	0.0368
Na in NaOH,	0.0058	0.0299	0.0361
	0.1709	0.1807	0.1804

It would appear from these results, therefore, that the oxi-

dation of sodium sulphide to sulphate by means of the alternating current is the same, so far as chemical changes are cerned, as oxidation by the direct current. The rate of oxidation, using platinum wire electrodes, is, of course, much slower with the alternating current than with the direct when large electrodes were used. However, if the electrolysis were continued long enough, there is no reason to suppose that all the sulphide in the electrolyte could not be oxidized to sulphate. In these experiments it was not considered advisable to carry an electrolysis beyond five hours, inasmuch as the platinum electrodes dissolved under the combined influence of the alternating current and electrolyte, which never happened when the direct current was employed. Some idea of the rapidity with which platinum dissolves under the above conditions can be obtained from a platinum determination made in Solution No. II. 100 cc. gave 0.0216 gram platinum. At the end of the electrolysis, therefore, the platinum electrodes weighed 0.216 gram less than at the beginning. Judging from the red color in the electrolytes and the precipitation of platinum sulphide when acids were added, sodium thioplatinate was produced. This part of the subject, however, needs further investigation.

TUFTS COLLEGE, MASS.,
MAY 11, 1896.

A METHOD FOR OBTAINING CRYSTALLINE SILICON.

BY G. DE CHALMOT.

In a recent number of this JOURNAL[1] I mentioned that a mixture of calcium silicide and crystalline silicon can be obtained in an electric furnace from a mixture of silica, calcium oxide, and carbon. The silicide in this mixture can be destroyed by heating with hydrochloric acid, after which the calcium chloride can be washed out, and the silicic acid dissolved in sodium carbonate solution. The crystalline silicon which remains contains some silicide of iron. I found it more convenient to remove the silicic acid with hydrofluoric acid. It is then also possible to dissolve most of the iron sili-

[1] Page 320.

cide, and I have reduced the amount of iron in the remaining silicon to 1 per cent.

The mixture of calcium silicide and silicon is lighter than the slag from which it is derived, which is seen from the following data:

Specific gravity of alloy.	Specific gravity of slag.
2.31	2.83
2.22	3.12

The metal has a tendency to move to the cathode, hence the yield in an upright furnace can be considerably increased by having the cathode for the upper pole. In this case gravity and electrolysis both tend to move the metal in the same direction, *viz.*, upward. It is necessary that the upper pole should be kept covered with the mixture in order to prevent the burning of the metal.

I have found that with purer materials it becomes harder to obtain calcium silicide, and that it is almost impossible to obtain any, if very little iron is present. For the formation of this silicide the presence of some iron seems to be essential.

The yield of calcium silicide and silicon is not large, and I have substituted other oxides of metals for calcium oxide, thereby considerably increasing not only the yield of silicide, but also of free silicon.

I again heated a mixture of oxide of metal, silica, and carbon with a direct current of low voltage and high amperage.

I thus obtained a mixture of silicide of iron and silicon with 69 per cent. of silicon. The copper silicide with 51.5 per cent. silicon and the silver silicide mentioned on page 96 of this volume are other products of the same method.

I have given more special attention to manganese because its silicide can easily be separated from the free silicon. I obtained from mixtures containing powdered quartz 40 parts, Mn_3O_4[1] 5 parts, charcoal 15 parts, calcium oxide 15 parts, two alloys, of which the following are partial analyses:

[1] Which contained some iron.

	I.	II.
Si	73.77	68.85
Mn	23.86	26.11
Fe	0.92	1.49
Ca	trace	1.82

I obtained from a mixture containing quartz 40 parts, Mn_3O_4 15 parts, charcoal 15 parts, calcium oxide 7.5 parts, an alloy which contained :

	III.
Si	57.23
Mn	40.31
Fe	2.81
Ca	trace

These alloys are crystalline and contain some well developed crystals which, however, can not be separated.

These alloys contain mainly silicide of manganese and crystalline silicon. They are slightly attacked by boiling dilute hydrochloric acid, more by strong hydrochloric acid, and energetically by cold hydrofluoric acid, which dissolves all the manganese silicide, leaving the silicon.

I treated a part of II with hydrofluoric acid for four days, renewing the acid four times after pouring off the old acid. I washed out the residue and boiled it with diluted hydrochloric acid in order to dissolve all the manganese salt, and I thus obtained a crystalline powder, which was free of manganese and contained 97.77 per cent. of silicon. The silicon was determined by melting it with a mixture of alkali carbonate and nitrate, and weighing the silica. The yield of silicon was 33 per cent., some having been lost with the acid that was poured off.

In order to obtain an idea of the composition of the manganese silicide which is present besides the free silicon, I treated 0.3933 gram of II with cold hydrofluoric acid in a platinum dish and extracted it three times, each time for twelve hours. Instead of pouring off the acid each time, I diluted it with water and filtered through a small ash-free filter and, after unfolding this, washed off into the platinum dish the silicon adhering to the filter, with a few drops of water. After boiling the residue with hydrochloric acid it

was collected on a weighed filter. It weighed 0.1610 gram = 40.94 per cent. of free silicon.

If we assume that the calcium and iron were present as the silicides, $CaSi_2$ and $FeSi_2$, we can calculate the amount of silicon united with the manganese.

Total silicon, 68.85 per cent.

	Per cent.
Silicon for 1.49 per cent. Fe	1.51
" " 1.82 " " Ca	2.57
Free silicon	40.94
	45.02

Silicon united with manganese, 23.83 per cent.

26.11 per cent. of manganese in the form of $MnSi_2$ would require 26.97 per cent., of MnSi 13.48 per cent., and of Mn_2Si 6.74 per cent. of silicon.

0.4558 gram of III was treated as stated above. The residue was 0.0575 gram = 12.62 per cent. free silicon.

The calculation for III is:

	Per cent.
Silicon for 2.81 per cent. Fe	2.84
Free silicon	12.62
	15.46

Total silicon 57.23 per cent.

Silicon united with manganese 41.77 per cent.

40.31 per cent. of manganese in the form of $MnSi_2$ requires 41.63 per cent., of MnSi 20.81 per cent., and of Mn_2Si 10.41 per cent. of silicon.

These calculations are subject to the following errors, which, however, partially neutralize each other:

1. The residue of silicon contains impurities, for example, some of the iron silicide.

2. In II there is probably some carborundum.

3. It may be that cold hydrofluoric acid does somewhat attack crystalline silicon if it acts for thirty-six hours. But these errors have hardly influenced the result to such an extent as to leave doubt as to the formula of the manganese silicide, which is in both samples $MnSi_2$.

This silicide differs from the silicide, Mn_3Si, of Vigoureux,[1] as it is not easily attacked by dilute acids. This result corresponds with that obtained with iron silicides where the silicide is attacked less readily if it contains more silicon.

WILLSON ALUMINUM CO.,
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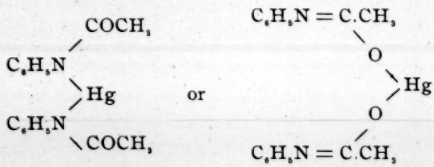
Contributions from the Sheffield Laboratory of Yale University.

I.—ON SOME MERCURY SALTS OF THE ANILIDES.

BY H. L. WHEELER AND B. W. MCFARLAND.

Numerous investigators have had occasion to work with the sodium and silver salts of the anilides and have used these compounds in syntheses, while little attention has been given to the mercury salts. Mercury acetanilide first prepared by Oppenheim and Pfaff[2] seems to be the sole representative of the mercury salts of the anilides that has been prepared. This compound has recently been examined by Piccinini,[3] and he concludes that it is a mercurammonium derivative, since the mercury can be removed from it at ordinary temperature by means of sodium thiosulphate, potassium iodide, or ammonium bromide, thus differing from Pesci's[4] paramercurioacetanilide, which is not effected by these reagents.

The experiments of Piccinini, however, do not decide whether mercury acetanilide has the structure



The former structure corresponds to that generally accepted for the sodium salts of the anilides, the latter to that of the silver salts.

We are now prepared to show that formanilide and paraformtoluide give mercury salts, and, that these salts—as well

[1] Compt. rend., **121**, 771. [2] Ber. d. chem. Ges., **7**, 624.
[3] Ber. d. chem. Ges., **28**, R. 113. [4] Ber. d. chem. Ges., **28**, R. 112.

as mercury acetanilide—react with benzoyl chloride as if they had the metal joined to nitrogen. We have also found that the action of bromine and iodine on mercury formanilide is similar to that of benzoyl chloride.

In the course of the above-mentioned reaction such mercuric halogen compounds as the following are directly obtained :

$$C_6H_5N\begin{matrix}CHO\\HgCl,\end{matrix} \qquad C_6H_5N\begin{matrix}CHO\\HgBr,\end{matrix} \qquad C_6H_5N\begin{matrix}CHO\\HgI.\end{matrix}$$

The reactions may be represented by the following equation in which hal represents halogen and X either C_6H_5CO—, Br, or I.

$$\left.\begin{matrix}C_6H_5N\begin{matrix}CHO\\Hg + hal\end{matrix}X\\C_6H_5N\begin{matrix}\\CHO\end{matrix}\end{matrix}\right\} = C_6H_5N\begin{matrix}CHO\\Hg\ hal\end{matrix} + C_6H_5N\begin{matrix}X\\CHO\end{matrix}$$

These halogen mercuric compounds represent a part of the mercuric salt united to halogen. They are undoubtedly nitrogen derivatives, being analogous to the well-known ammonia compound H_2N—HgCl, the so-called white precipitate, and to the aniline salts, $C_6H_5N<^{H}_{HgCl(Br)\,(or\ I)}$, $C_6H_5N<^{H}_{HgOCOCH_3}$, etc., described by Pesci.[1]

It is also to be noticed that in the above-mentioned reactions of the mercury salts, besides the halogen mercury compounds, nitrogen-substituted anilides are also formed. For example : Benzoyl chloride and mercury formanilide give formylbenzanilide, $C_6H_5N<^{CHO}_{COC_6H_5}$, in addition to chlormercury formanilide, $C_6H_5N<^{HgCl}_{CHO}$; and the diacid anilide when treated with alkali or dilute acid is decomposed into benzanilide, $C_6H_5N<^{H}_{COC_6H_5}$, and formic acid. The diacid anilide, therefore, has both acid groups attached to nitrogen, since such a decomposition could only result from a nitrogen

[1] Gazz. chim., **22**, [1], 378.

derivative, *i. e.*, $C_6H_5N<^{CHO}_{COC_6H_5}$. On the other hand, if the diacid anilide were an oxygen derivative, *i. e.*,

$$C_6H_5N=C<^{H}_{O.COC_6H_5},$$

it is evident that the formyl group could not be removed without also removing the benzoyl radical, and we should get aniline, formic and benzoic acids instead of benzanilide. The decomposition of the diacid anilide, therefore, is to be represented as follows:

$$C_6H_5N\begin{matrix}\diagup\ \boxed{CHO}\\ \diagdown\ COC_6H_5\end{matrix}\ \boxed{+\ HO}H = C_6H_5N\begin{matrix}\diagup\ H\\ \diagdown\ COC_6H_5\end{matrix} + HOCHO$$

The above facts show that the mercury salts of the anilides have the mercury undoubtedly united to nitrogen, for were it joined to oxygen, it would be impossible to explain the formation of the halogen mercury compounds and the diacid anilides by the usual theory, in tautomeric reactions, of addition and separation, since in this case an assumption of an elaborate rearrangement would also be necessary.

The mercury salts are therefore to be represented by the following structure:

$$C_6H_5N\begin{matrix}\diagup\ CHO\\ \diagdown\ Hg\\ \diagup\ CHO\\ C_6H_5N\end{matrix} \quad \text{and not} \quad C_6H_5N=C\begin{matrix}\diagup\ H\\ \diagdown\ O\\ \\ O\\ \diagup\ H\\ C_6H_5N=C\end{matrix}\ \begin{matrix}\\ \\ \diagdown\\ Hg\\ \diagup\\ \\ \end{matrix}$$

Experimental Part.

Mercury Formanilide, $(C_6H_5NCHO)_2Hg$, is most conveniently prepared by dissolving formanilide and mercuric bromide in alcohol, then adding the calculated quantity of sodium ethylate, and diluting with water. The resulting precipitate [Analysis I] can be crystallized from water [Analysis II]. It then separates in colorless needles which melt at about 194°. Mercury formanilide can also be obtained by use of mercuric nitrate and sodium ethylate, or by boiling an alcoholic solution of formanilide with mercuric oxide [Analy-

sis III] or mercurous oxide [Analysis IV]. It also results when sodium formanilide is boiled with mercurous nitrate.

	Found.				Calculated for $C_{14}H_{12}N_2O_2Hg$.
	I.	II.	III.	IV.	
Hg	45.0	45.2	46.1	45.4	45.4
N		6.2			6.3

Chlormercury formanilide, $C_6H_5N<\begin{matrix}CHO\\HgCl\end{matrix}$. — When mercury formanilide is suspended in benzene, and one molecule of benzoyl chloride is added the reaction takes place, slowly in the cold, rapidly when warmed. On filtering and washing the residue with benzene, pure chlormercury formanilide remains [Analysis I]. This compound is also obtained when equal molecules of formanilide, mercuric chloride, and sodium ethylate are mixed in alcoholic solutions [Analysis II]. It crystallizes from water in shining colorless plates melting at 191° [Analysis III].

	Found.			Calculated for $C_7H_6NOHgCl$.
	I.	II.	III.	
Hg		56.4	56.5	56.3
Cl	9.6	9.9		9.9

Formylbenzanilide, $C_6H_5N<\begin{matrix}CHO\\COC_6H_5\end{matrix}$. — On concentrating the above-mentioned benzene solution, this diacid anilide is obtained in colorless, brittle prisms, which on recrystallizing from benzene melt at 112°. It crystallizes from water in needles, and when recrystallized from this solvent or from alcohol the melting-point does not change. Analysis gave:

	Found.	Calculated for $C_{14}H_{11}NO_2$.
C	75.27	74.67
H	4.93	4.88
N	6.1	6.22

When formylbenzanilide is treated with acids or alkalies, the formyl group is removed and benzanilide is formed. This was identified by its melting-point and general properties. It is to be noticed that this diacid anilide from mercury formanilide is identical in all its properties with formyl benzanilide obtained from silver formanilide and benzoyl chloride.[1]

Brommercury formanilide, $C_6H_5N<\begin{matrix}CHO\\HgBr\end{matrix}$, was obtained

[1] This JOURNAL, **18**, 381.

when mercury formanilide was suspended in carbon disulphide and 1 molecular proportion of bromine added. During this operation the whole was cooled with ice. The residue was washed with carbon disulphide until colorless, dried in the air, and then analyzed [Analysis I]. Another portion was crystallized from dilute alcohol from which it separated in bunches of radiating, yellow-white plates. The trace of color and the analysis indicate that in this operation a slight decomposition had taken place [Analysis II].

	Found.		Calculated for $C_7H_6NOHgBr$.
	I.	II.	
Hg		50.2	50.0
Br	19.9	19.4	20.0

The above-mentioned carbon disulphide solution was evaporated over sulphuric acid by means of a pump. This left a brown or black mass. The color was not removed from the solution in carbon disulphide or ether by boiling with animal charcoal. Attempts to isolate the unstable formylbromaminobenzene[1], $C_6H_4N<^{Br}_{CHO}$, were therefore abandoned. We then boiled the residue with water. This extracted a colorless substance containing bromine, crystallizing in needles from hot water and melting at 119°. It was, therefore, the expected parabromformanilide, resulting probably from the molecular rearrangement of formylbromaminobenzene.

Iodmercury formanilide, $C_6H_4N<^{CHO}_{HgI}$.—Molecular proportions of mercury formanilide and iodine were mixed in carbon disulphide, and the whole was allowed to stand for twenty-four hours. The residue which remained was filtered, washed with carbon disulphide, dried, and analyzed. It decomposed on boiling with water.

	Found.	Calculated for C_7H_6NOHgI.
I	28.5	28.4

The carbon disulphide filtrate from iodmercury formanilide was evaporated to dryness at ordinary temperature. A black residue resulted as in the case of the bromine reaction. From

[1] Slosson: Ber. d. chem. Ges., **28**, 3268.

this residue we succeeded in extracting a small amount of paraiodformanilide by boiling with water. On crystallizing from water it gave the correct melting-point, 108°.

In another experiment chloroform was used instead of carbon disulphide, and an excess of mercury formanilide was present. We succeeded in this experiment in showing the presence of a substance which easily liberated iodine, but which was not obtained in pure condition. This unstable compound was probably iodisoformanilide or formyliodaminobenzene which Comstock and Kleeburg[1] obtained from the silver salt of formanilide. On warming this with formic acid, then crystalling from water as they describe, we obtained paraiodformanilide, crystallizing from water in colorless needles, aud melting at 108°.

Mercury formanilide acetate, $C_6H_5N<^{CHO}_{HgOCOCH_3}$.—When mercuric acetate is mixed with formanilide in alcoholic solution, acetic acid is liberated. On concentrating the solution bunches of colorless slender prisms of the above compound separate. Again, on dissolving dry mercuric acetate in a very strong alcoholic solution of formanilide and then warming, the whole suddenly solidifies. When this mass is crystallized from strong alcohol the same colorless prisms result :

	Found.	Calculated for $C_9H_9NO_3Hg$.
Hg	53.1	52.8

Mercury formparatoluide, $(CH_3C_6H_4NCHO)_2Hg$. — Ten grams of formparatoluide and 14 grams of mercuric bromide were dissolved in 40 cc. of 95 per cent. alcohol, then 1.7 gram of sodium also in 40 cc. of alcohol were added. This, on shaking, gave a clear solution, to which an equal volume of water was added. The mercury salt then separated in a thick mass of crystals. These were washed with alcohol [Analysis I]. A portion crystallized from water gave colorless needles [Analysis II]. Another specimen was prepared by using mercuric chloride instead of the bromide, and this was crystallized from 50 per cent. alcohol and analyzed [Analysis III].

[1] This JOURNAL, **12**, 493.

	Found. I.	Found. II.	Found. III.	Calculated for $C_{14}H_{13}N.O_2Hg$.
Hg	43.48	43.25	43.00	42.73

Chlormercury formparatoluide, $CH_3C_6H_4N<\begin{matrix}CHO\\HgCl\end{matrix}$. — This was obtained as a residue when the above mercury salt, suspended in benzene, was treated with benzoyl chloride [Analysis I]. It crystallizes from water in colorless needles, and the analysis indicates that in this treatment a slight decomposition takes place [Analysis II].

	Found. I.	Found. II.	Calculated for $C_8H_8NOHgCl$.
Hg	54.19	52.53	54.20

Formylbenzparatoluide, $CH_3C_6H_4N<\begin{matrix}CHO\\COC_6H_5\end{matrix}$.—The benzene solution from chlormercury formparatoluide was evaporated, and the residue taken up in ether. This operation was repeated. The material was then crystallized from a mixture of ligroïn and ether, when colorless prisms were obtained melting at 101°.

	Found.	Calculated for $C_{15}H_{13}NO_2$.
N	5.36	5.85

On warming this product with dilute sodium hydroxide, the formyl group was removed and benzparatoluide was obtained.

Acetbenzanilide, $C_6H_5N<\begin{matrix}COCH_3\\COC_6H_5\end{matrix}$.—The preparation of this compound was perfectly analogous to that of formylbenzanilide and formylbenzparatoluide. Mercury acetanilide, best prepared according to the directions of Piccinini,[1] and benzoyl chloride were mixed in molecular proportions in benzene. On filtering, evaporating the benzene solution, and crystallizing the residue from dilute alcohol, an oil separated which changed to long needles, melting at 68°. When this material was crystallized three times from dilute alcohol the melting-point remained constant.

	Found.	Calculated for $C_{15}H_{13}NO_2$.
N	5.81	5.85

On warming with dilute sodium hydroxide and then crystallizing from alcohol, pure benzanilide was obtained, melting

[1] *Loc. cit.*

from 162° to 163°. Here, also, as in the case of formylbenzanilide and formylbenzparatoluide, alkali removes the lower acid group.

Mercury symmetrical tribromacetanilide, $(C_6H_2Br_3NCOCH_3)_2Hg$.—This was prepared like mercury acetanilide, except that dilute alcoholic solutions were used. The precipitate, washed with water and then with alcohol, gave on analysis 22.4 per cent. of mercury instead of 21.4 per cent. It crystallizes from 50 per cent. alcohol in bunches of needles.

Mercury formyl-α-naphthylamine, $(C_{10}H_7NCHO)_2Hg$.—This was prepared like mercury formparatoluide. It gave colorless needles, which were washed with water, and then with hot alcohol. A mercury determination gave 36.4 per cent. mercury instead of 37.6 per cent.

It will be noticed that, as the solubility of the anilide in water or dilute alcohol decreases, pure mercury salts are to be obtained only with difficulty. For this reason acetparatoluide and benzanilide did not give mercury salts of even approximate purity by the above methods.

NEW HAVEN, May, 1896.

II.—ON THE USE OF ANTIMONY TRICHLORIDE IN THE SYNTHESIS OF AROMATIC KETONES.

BY WILLIAM J. COMSTOCK.

Among the reagents which may be used in special cases instead of aluminium chloride in syntheses involving the separation of hydrochloric acid, there is no record, as far as I have found, of the use of antimony trichloride. Indeed the applicability of aluminium chloride is so general that one would hardly search deliberately for a condensing-agent to replace it, although its use does involve certain objectionable features on account of its extremely hygroscopic properties. It is certainly more agreeable to handle antimony trichloride, which has moreover comparative cheapness in its favor, as well as the advantage that in case it has absorbed moisture by long standing or exposure, the anhydrous chloride can be readily recovered. Should it be a question of working on a large scale where the expense is the important, perhaps the

one essential, consideration, the use of antimony trichloride would undoubtedly be preferred, as it can be recovered from the product of the reaction by evaporation of the hydrochloric acid solution used to free the ketone from antimony, and subsequent distillation of the residue. I have found that a mixture of an acid chloride with an aromatic hydrocarbon and antimony trichloride, evolves hydrochloric acid when heated, and that for the synthesis of benzophenone and its homologues the method can be used with excellent results. The yields compare favorably with those obtained by Elbs[1] who made a careful study of the Friedel and Crafts reaction for the synthesis of the same ketones. The reaction does not take place at ordinary temperature and cannot be successfully applied with low-boiling chlorides, as, for instance, to the synthesis of acetophenone. It is not my intention to work through the list of ketones to whose synthesis the method might be applied; but I give experiments in three typical cases, leading to well known compounds, to show the yields, advantageous proportions, etc. Without doubt the method can be used to condense any acid chloride having a moderately high boiling-point, with an aromatic hydrocarbon. For the preparation of ketones from the phenol ethers the method can be used, but its advantages are rather doubtful on account of the saponifying action of the antimony trichloride.

Gattermann, Ehrhardt and Maisch[2] have made many ketone syntheses with the phenol ethers according to the method of Friedel and Crafts but as the yields are not given, I have no means of comparing the two condensing-agents.

Hartmann and Gattermann[3] have shown that the phenol ethers are saponified by aluminium chloride, and state that this causes a loss in the preparation of the ketones. The saponifying action of antimony trichloride on the phenol ethers reduces the yield of ketone far below that found in the experiments with hydrocarbons given below, although the reaction takes place more readily. I have obtained about 40 per cent. of the theoretical yield of pure *p*-methoxybenzophenone, and doubtless the yield could be improved by a careful

[1] J. prakt. Chem., **35**, 465. [2] Ber. d. chem. Ges., **23**, 1199.
[3] *Ibid.*, **25**, 3531.

study of the conditions. Indeed, by diluting with carbon bisulphide the amount of bye-products is reduced, but the time required is much longer. As to the use of antimony trichloride for the synthesis of compounds other than ketones, I have made no careful study, but will mention a few observations that seem of interest in this connection. It is not possible to prepare triphenylmethane from chloroform by this method; there is no evolution of hydrochloric acid when chloroform, benzene and antimony trichloride are heated, even when large quantities of chloride are used. The reaction between benzal chloride and benzene seems to take place very readily, but the product contains a large amount of dark resinous matter, and so much that is not triphenylmethane that I have not studied the case further.

Syntheses with benzyl chloride in presence of antimony trichloride are not to be recommended. To be sure, diphenylmethane can be prepared with a yield of about 12 per cent., but the greater part of the benzyl chloride is converted into more complicated, high-boiling compounds, apparently the same anthracene derivatives that are formed when benzyl chloride is treated with aluminium chloride. In consideration of the possibility, though a remote one, of a direct synthesis of the ethereal salts from ethyl chlorcarbonate, I have made one experiment, with paraxylene. But the result showed that the reaction takes place in the same way as with aluminium chloride, *i. e.*, carbonic acid is given off together with the hydrochloric acid, and the product of the reaction is a mixture of unaltered paraxylene with higher-boiling hydrocarbons, but no ethereal salt.

Smith and Davis[1] have described addition-products of antimony trichloride with benzene and napththalene, compounds having the composition of two molecules of hydrocarbon to three molecules of antimony trichloride, and it is worth mentioning that aluminium chloride and antimony trichloride are the two metallic chlorides with which "molecular"-compounds of the aromatic hydrocarbons have been obtained. Whether this has any connection with the syntheses which can be carried out in presence of these chlorides is doubtful.

[1] J. Chem. Soc., 41, 411.

Experimental.

In conducting the operation, the mixture is heated in a flask with reflux-condenser, either by a direct flame, or better by means of a paraffin or other bath. The only precautions to be taken are to use substances free from water, to protect the mixture from the moisture of the air during the operation by means of a calcium-chloride tube, and to avoid raising the temperature too rapidly during the early part of the operation. The evolution of hydrochloric acid is rapid at 140°. This is true in the cases given below, as well as in other cases where the reaction was tried as a test-tube experiment only, without working up the product. The temperature of the bath is gradually raised as high as 200°. When the evolution of gas stops, and the odor of the acid chloride has disappeared, the mixture is washed with strong hydrochloric acid in a separatory funnel until the antimony is entirely removed. The ketone is then taken up in ether, dried over potassium carbonate, and finally distilled. Should there be difficulty in getting the ketone to separate from the acid solution, it can be taken up in ether at once, but in this case it requires repeated shaking of the ethereal solution with hydrochloric acid to remove the antimony trichloride. In carrying out the reaction with small quantities it is, however, desirable to take up in ether at once. For removing the antimony trichloride from the ketones it is also possible to use a strong solution of potassium or calcium chloride, acidified with hydrochloric acid.

Benzophenone.

Benzoyl chloride reacts more slowly with benzene than it does with the higher hydrocarbons. It is impossible to carry out the reaction with a small proportion of antimony trichloride, as the temperature of the mixture cannot be raised sufficiently high. With 56 grams of benzoyl chloride, 32 grams of benzene, and 75 grams of the trichloride, the reaction required forty hours for its completion. The yield of pure benzophenone, boiling at 306–308°, was 51 grams or 70 per cent. of the theoretical. The proportions given in the following experiment are to be recommended, as they enable

one to carry out the reaction within reasonable time limits:

112 grams C_6H_5COCl.
70 grams C_6H_6.
300 grams $SbCl_5$.

The reaction was completed in about twelve hours. The yield was 108 grams of benzophenone boiling at 306–308°, *i. e.*, 74 per cent. of the theoretical.

The yield of crystallized, but not carefully rectified, ketone is of course larger. Elbs gives the yield of "pure crystallized ketone," obtained by the Friedel and Crafts reaction, as 70 to 75 per cent. of the theoretical.

Benzoyl Chloride and Toluene.

Experiment 1.—The mixtnre used was made up thus:

56 grams C_6H_5COCl.
40 grams C_7H_8.
15 grams $SbCl_5$.

The time required to complete the reaction was forty-two hours. The yield of mixed ortho- and paratolylphenyl ketones, 56 grams or 72 per cent. of the theoretical, boiling between 177° and 182°, at a pressure of 16 mm.

Experiment 2.—The mixture used in this case was:

56 grams C_6H_5COCl.
40 grams C_7H_8.
60 grams $SbCl_5$.

The reaction was completed in five hours; yield of mixed ortho- and para-ketones, 62 grams, or 80 per cent. of the theoretical. According to Elbs, the yield of mixed ortho- and paraketones runs up as high as 95 per cent. of the theoretical, when aluminium chloride is used. As to the porportion of ortho and para in the mixture, there is apparently a higher percentage of ortho-ketone formed when antimony trichloride is used. Elbs states that from his mixture of the two ketones he could obtain 80 to 95 per cent. of pure paratolylphenyl ketone, and that the mixture "caked" at ordinary temperature. I obtained 64 per cent. of pure para-ketone from the mixture. The separation is of course incomplete, but the mixture of ketone, which I obtained, did not "cake" till it was cooled with ice.

Paraxylylphenylketone.

The following mixture was used:

28 grams C_6H_5COCl.
22 grams paraxylene.
20 grams $SbCl_5$.

The reaction was completed in about six hours. The yield of pure ketone, boiling between 317–319°, was 34 grams, or 80 per cent of the theoretical.

In another experiment the same amounts of benzoyl chloride and paraxylene were used with 30 grams of the trichloride. The reaction was completed in 4½ hours; yield 31 grams, or 74 per cent. of the theoretical. Elbs obtained 60 to 70 per cent.

NEW HAVEN, May, 1896.

Contributions from the Laboratory of General Chemistry, University of Michigan.

I.—THE ACTION OF SODIUM ON ALDEHYDE.

BY PAUL C. FREER.

Some years ago I demonstrated that acetone gives a well defined sodium derivative from which both *o* and *c* acyl bodies can be obtained by the action of benzoyl chloride[1], and the proof that sodium acetone is a substance of the structure

$$CH_3.CONa : CH_2$$

was furnished by this means, as well as by the action of ethyl chlorcarbonate.[2] This work showed the previously accepted theory that only those ketones could form sodium derivatives in which the grouping—$CO.CH_2$—or—CO.CHR—is in proximity to negative radicles, to be without foundation. It seemed interesting, therefore, to discover if aldehyde would behave in a similar manner and form sodium aldehyde when brought in contact with metallic sodium. The problem, however, offered greater difficulties because of the well known ease with which aldehyde enters into the formation of condensation-products in the presence of dehydrating agents. The result proved that my expectation was correct: pure

[1] This JOURNAL, 15, 582. [2] *Ibid*, 13, 22: 17, 1.

aldehyde[1] reacts violently with sodium so that dilution with absolute ether and cooling is imperative; a white crystalline sodium derivative is formed and a gas is evolved, which careful analysis proved to be pure hydrogen.[2]

During this reaction air must be rigidly excluded, for the products are easily attacked thereby. The sodium compound, under any circumstances, begins to turn yellow after a few minutes, and soon changes to a brown, sticky mass, which it is impossible to filter. An analysis is of course out of the question. Owing to this rapid polymerization it was impossible to obtain well-defined products by the action of benzoyl chloride as was the case with acetone, a thick resin resulting which did not invite further investigation. This means of advance, however, was not necessary, as a slight experimental *detour* gave most satisfactory results, and afforded an insight into the constitution of the sodium derivative, which left nothing to be desired. This method—which I intend to investigate as to its general applicability—consisted in the action of sodium upon a mixture of benzoyl chloride and aldehyde.

The Action of Sodium on Benzoyl Chloride and Aldehyde.

Aldehydoaldol Benzoate.—1.5 grams of sodium in a flask with inverted condenser are covered with 150 cc. of absolute ether, the air is expelled by means of dry hydrogen and then a mixture of 9.1 grams of benzoyl chloride with an excess of aldehyde, is slowly run in, the flask being kept cool throughout.[3] An immediate reaction sets in, hydrogen is evolved, and sodium chloride separates. After the action is complete, and the odor of benzoyl chloride has disappeared, the ethereal solution is washed with water and small quantities of a dilute solution of caustic potash, until all benzoic acid is removed.

[1] All of the aldehyde used in this and subsequent experiments was carefully fractioned; its boiling-point was 19–20°. In the preliminary experiments this product was further shaken with phosphorus pentoxide, poured off, and refractioned so that no moisture was present. Subsequently this precaution was abandoned as unnecessary.

[2] Beckmann and Paul [Ann. Chem. (Liebig) **266**, 281] have tried the action of benzaldehyde on sodium. The brief mention of their results shows that they obtained sodium hydrobenzoin thereby. This action is entirely different from that of sodium in acetaldehyde, as the following work will show.

[3] I convinced myself that pure benzoyl chloride has no action on sodium.

It is then dried over sodium sulphate and the ether evaporated in a vacuum. There results a thick, slightly yellow syrup, which soon becomes permeated with a mass of prismatic crystals. When the quantity of the latter no longer increases, they are filtered out—an operation which takes a long time, even with the best of vacuum pumps—spread on a porous plate and then recrystallized from as small a quantity of alcohol as possible. The product is a white, crystalline solid, separating from ligroïn in large shiny prisms, tolerably soluble in alcohol, soluble in benzene and chloroform, insoluble in water; melting-point 86–87°. The results of the analyses were as follows:

	Calculated for $C_{13}H_{14}O_4$. Per cent.	Found. I.	II.
C	66.1	65.9	65.36
H	6.71	6.9	7.04

A molecular-weight determination according to the cryoscopic method, in benzene solution, gave the following results:

Solvent.	Substance.	*D.*	*M.*
20.2617	0.0477	0.05	256.9
"	0.0974	0.10	236.0
"	0.1515	0.16	229.5
"	0.2333	0.24	235.5

The calculated molecular weight is 236. It will be observed that there is no increase in the molecular weight with increasing concentration, which renders it probable that no hydroxyl group is present, for Auwers has shown[1] that many hydroxylated bodies give an increase in the molecular weight as the amount of substance in unit weight of solvent is increased. The formula obtained is that which would result from one molecule of benzoate of aldol and one of aldehyde. The constitution of the body is proved by the following results:

Decomposition of the Compound, $C_{13}H_{14}O_4$, by Water at 100°.

7 grams of the pure body and 10 grams of water were sealed in a tube and heated for one and one-half hours at 100°. On

[1] Ztschr. phys. Chem., **12**, 689; **15**, 33.

cooling no pressure was observed and the liquid was permeated with crystals of benzoic acid (3.5 grams). The latter was filtered out, dissolved in sodium carbonate, reprecipitated, and a melting-point of 121° obtained. There remained 0.7 gram of a thick syrup insoluble in sodium carbonate and probably identical with the oil originally formed by the action of benzoyl chloride and aldehyde on sodium, and from which the crystals of aldehydoaldol benzoate had been filtered. The clear aqueous solution, which had a strong odor of aldehyde and from which the benzoic acid had been separated, was repeatedly extracted with pure ether, dried over sodium sulphate, and the ether distilled. There remained a thick syrup (1.5 grams) which was fractioned *in vacuo*. It had a boiling-point of 87° at 28 mm., was perfectly soluble in water, reduced an ammoniacal solution of silver nitrate, gave a strong odor of crotonic aldehyde when heated at ordinary pressures —in short it was aldol. The ether which had been distilled from the original solution, on saturation with dry ammonia, produced aldehyde ammonia in small quantity. The decomposition-products of the compound, $C_{13}H_{14}O_4$, with water are therefore benzoic acid, aldol, and aldehyde.

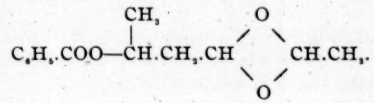
Distillation of the Compound, $C_{13}H_{14}O_4$.

All attempts to distill the solid unchanged, even in a vacuum, failed, because decomposition set in long before the boiling-point was reached. As the products of destructive distillation are of the greatest importance in determining the constitution of the body, 11.2 grams of the pure solid were placed in a distilling-flask connected with a condenser and jacketed receiver, filled respectively with ice-water and a freezing-mixture, and the decomposition was carried on over a free flame. A colorless liquid passed over between 80° and 120°, and when all of this had distilled the thermometer rapidly rose to 240°, and the distillate then solidified in the condenser. This solid was benzoic acid. The liquid was carefully fractioned, first on a water-bath, then on an oil-bath. A low-boiling, colorless fluid passed over below 38°, and this, on refractioning, boiled at 21–22°; it had the odor of aldehyde, reduced silver nitrate, and

promptly formed aldehyde-resin with a solution of caustic potash, and was therefore pure acetaldehyde. After all the latter had been driven over, the remainder distilled between 85° and 106°. A small portion passed over below 90°. This consisted of crotonic aldehyde and a little of a lower-boiling body which on oxidation yielded in part isocrotonic acid and which therefore contained isocrotonic aldehyde. The major portion boiled between 104° and 105° (2.2 grams). This liquid had the well-known odor of crotonic aldehyde and, on oxidation with moist silver oxide, and recrystallization from ligroïn, produced pure solid crotonic acid with a melting-point of 71°. The products of destructive distillation are, therefore, benzoic acid, crotonic aldehyde, and acetaldehyde. The same result is observed if the solid body is heated with dilute hydrochloric acid for one hour at 100°; benzoic acid, crotonic aldehyde and acetaldehyde being formed. When heated in a pure state in a sealed tube the body breaks down into the same products at 150°. Boiling with alcohol very slowly produces benzoic ether.

The solid of the formula, $C_{13}H_{14}O_4$, is insoluble in cold dilute caustic potash or in alkaline carbonates; on warming it dissolves, the solution turns yellow, and aldehyde resin is produced, a portion of the solid separating on cooling, if the heating process has not been carried too far. It does not react with bromine in chloroform solution, is not attacked by cold potassium permanganate solution, and does not react with phenylhydrazine. In preparing the body, care must be taken to have exactly enough sodium and benzoyl chloride in the reacting mixture so that both are completely altered: an excess of ether prevents the formation of the solid and produces only the thick syrup mentioned above; an excess of aldehyde is also necessary. The absence of the solid, when the conditions of the reaction are not accurately adhered to, is of course due to the extreme ease with which it is decomposed by acids and alkalies. Even on standing in moist air, crystals of benzoic acid gradually form, extending out from the original body in sharp, shiny needles, which are easily distinguished.

The above results demonstrate clearly that the solid body is a benzoic ester of aldol, in which, however, the aldehyde grouping has disappeared, and at the same time the analyses and decomposition-products show that there also is acetaldehyde in the substance. In order to account for these facts it is necessary to assume that the latter substance is joined to the molecule in some such manner as it is in paraldehyde, *i. e.*, by means of oxygen. The only structural formula which fulfills the conditions is therefore



This acetal-like linking of acetaldehyde is similar to that observed by Schultz and Tollens[1] in their work on the action of formaldehyde on polybasic alcohols. This formula accounts for all of the reactions—the easy decomposition into benzoic acid, aldol, and aldehyde by water; the breaking down into benzoic acid, crotonic aldehyde, and aldehyde on destructive distillation; the formation of aldehyde resin on heating with potash; the indifference toward bromine, etc. The solid body, $C_{13}H_{16}O_4$, is therefore aldehydoaldol benzoate.

Constitution of Sodium Aldehyde and Formation of Benzoyl-Aldol Derivatives.

As has been mentioned, sodium acts on aldehyde, liberating hydrogen and producing a white crystalline body, which, however, in a very few minutes breaks down, giving a thick resin. On the other hand, the action of sodium on a mixture of aldehyde and benzoyl chloride produces bodies which contain the benzoyl group attached to oxygen. This demonstrates that in the sodium derivative which is at first formed the sodium is also attached to oxygen. Two possibilities present themselves: one, that the metal condenses aldehyde to aldol, and that the sodium derivative of the latter body is the first product; the other, that sodium aldehyde is first formed, the latter body then generating the higher condensation-products,

[1] Ann. Chem. (Liebig), **289**, 20.

which stop at aldol if benzoyl chloride is present to form stable derivatives, but which go farther if no such medium is present.

The latter view is the correct one, because sodium, in contact with aldol, acts in a manner entirely different from the way it does on aldehyde. No solid separates for some time after bringing sodium in contact with aldol, the reaction going on to form a soluble sodium aldol, which finally precipitates in part as a white crystalline solid. The latter rapidly turns yellow but even after twenty-four hours it remains as a powder, entirely different from the sticky mass obtained from aldehyde. Sodium aldehyde is therefore produced by the action of sodium on aldehydes and the reactions given above demonstrate that the sodium is attached to oxygen, so that sodium aldehyde is really *sodium vinyl alcohol*—$CH_2 : CHONa$.

This substance is only capable of a brief existence, for it soon decomposes, forming high molecular condensation-products (such as aldehyde-resin). In the presence of benzoyl chloride the condensation, owing to the production of a stable body, stops with aldol, the latter being produced either by addition of aldehyde to sodium aldehyde,

$$CH_2 : CHONa + HCH_2.CHO = CH_2.CHONa.CH_2.CHO,$$ and

$$CH_2.CHONa.CH_2CHO + ClCO.C_6H_5 = CH_2.CHO.CO.C_6H_5.CH_2CHO + NaCl;$$

or by the addition of aldehyde to vinyl benzoate,

$$C_6H_5.COO.CH : CH_2 + HCH_2.CHO = CH_2.CHO.CO.C_6H_5.CH_2.CHO.$$

The first view is the more likely, and this demonstrates that the first step toward the formation of aldehyde-resin consists in the production of aldol in the presence of alkaline condensation-agents. This is also shown by the fact that aldehyde-resin is readily produced from aldol by warming with a solution of caustic potash. If an excess of aldehyde is present, the aldol benzoate which is at first formed by the action of sodium is further in part condensed to produce the solid $C_{13}H_{14}O_4$:

$$CH_3.CHO.CO.C_6H_5.CH_3.CHO + CH_3.CHO = CH_3.CHO.CO.C_6H_5.CH_3.CHO_2.CH.CH_3.$$

These views are further borne out by a study of the thick syrup which is produced simultaneously with the solid.

The Liquid Product of the Action of Sodium on a Mixture of Benzoyl Chloride and Aldehyde : Action of Phenylhydrazine.

The fluid portions of the reaction-products which, as was mentioned above, constitute a thick syrup with a disagreeable odor resembling that of aldehyde, on standing, gradually deposit crystals of benzoic acid, although the ethereal solution from which they came was thoroughly shaken with sodium carbonate before evaporating. This decomposition goes on continuously so that the oily product must be used promptly in order to obtain the best results. This oil instantly takes up bromine in chloroform solution, with the separation of benzoic acid and the formation of a brominated thick oil which remains after filtering and which was not further investigated. Phenylhydrazine acts most readily. If the thick syrup is dissolved in absolute ether and an excess of phenylhydrazine is slowly added, a crystalline precipitate separates in fine silky needles. This is filtered, washed with ether and recrystallized, first from benzene and finally from hot alcohol, from which it separates in large shiny concentric plates, melting at 166–167°. The analyses gave the following results:

	Calculated for $C_{13}H_{12}N_2O$.	Found. I.	II.	III.
C	73.57	73.81	....	....
H	5.66	5.92	....	....
N	13.2	.....	13.7	13.5

The properties and combustion, therefore, agreed with monobenzoyl phenylhydrazine, so that decomposition had taken place. No other solid body could be separated from the mother-liquors, which, however, finally changed to a nearly solid mass of monobenzoyl phenylhydrazine, permeated by a thick resinous hydrazone. I at first thought that the

monobenzoyl phenylhydrazine owed its origin to free benzoic acid, which might have separated by decomposition even after all dissolved acid had been removed by sodium carbonate, but I soon convinced myself that benzoate of phenylhydrazine (melting-point 80–82°) does not change into benzoyl phenylhydrazine even by those means which are generally employed to obtain the hydrazides of the acids of the fatty series. Thus, when distilled *in vacuo* it gives off aniline, benzoic acid, and ammonia, and it does not change when heated in a sealed tube at 130° for six hours; at a higher temperature decomposition sets in. It is certain, therefore, that the oily product of the action of sodium on benzoyl chloride and aldehyde is decomposed by phenylhydrazine, separarating the benzoyl group to form monobenzoyl phenylhydrazine, and the oily hydrazones of the aldehyde with which the benzoic acid was united. This easy decomposition demonstrates beyond a doubt that the benzoyl group was attached to oxygen in the liquid, just as was proved to be the case with the solid product of the reaction. A similar splitting off of the benzoyl group as benzoyl phenylhydrazine was observed by Nef in the case of his β-benzoylisocrotonic ester.[1] From this result it seemed highly probable that the oil was aldol benzoate, and in order to prove this point the destructive distillation of the syrup was resorted to.

Distillation of the Liquid Product of the Action of Sodium on Benzoyl Chloride and Aldehyde.

This operation resulted as did the decomposition of the solid, with the exception that only a very small quantity of aldehyde, no more than is generally observed on boiling aldol itself, was recovered. All attempts to fraction the syrup without decomposition, even at a pressure of 2 mm., failed. As a consequence, about 20 grams of the thick syrup were distilled at ordinary pressures, while every precaution was taken to retain all of the low-boiling products. Decomposition readily sets in, and a colorless liquid passes over between 90° and 130°, the thermometer then rapidly rises, and finally

[1] Ann. Chem. (Liebig), 276, 203.

there is left benzoic acid, mixed with some aldehyde-resin. The low-boiling product was refractioned, a very little acetaldehyde passed off, then a considerable quantity of a mixture between 75° and 90° which could be further separated into a little acetaldehyde and much crotonic aldehyde, with some substance boiling at 83° to 87°. The latter kept getting less, however, at each redistillation, yielding more crotonic aldehyde, so that finally the attempt to isolate a pure product was abandoned and the part boiling between 75° and 100° was oxidized with silver oxide. I obtained in this way, after acidifying and repeated extraction with pure ether, mostly solid crotonic acid, but there was also present a liquid acid which had the pronounced odor of isocrotonic acid, and which, on conversion into the potassium salts, showed the characteristic needles of potassium crotonate along with the imperfectly crystalline knobs of the isocrotonate. The lower-boiling liquid therefore contained some of the long-sought isocrotonic aldehyde, although the quantity was too small to isolate and analyze, and it probably also suffered change on each distillation. It is likely that a careful preparation of crotonic aldehyde according to the usual method (from aldol) will also show some isocrotonic aldehyde, and I intend to look for this body when the return of cold weather renders successful work in this direction possible. The liquid boiling between 100° and 106° gave pure, solid crotonic acid on oxidation. It seemed almost certain from these results that the thick syrup which I had distilled was aldol benzoate, and in order to prove this point I prepared the latter body from aldol, sodium, and benzoyl chloride.

The Action of Benzoyl Chloride on Aldol and Sodium.

10.7 grams of freshly distilled, pure aldol (b. p., 87° at 28 mm.) were mixed with 17 grams of benzoyl chloride and diluted with two volumes of absolute ether and this solution was added to 2.8 grams of sodium, covered with 100 cc. of the same medium. Reaction set in at once, hydrogen was evolved, and sodium chloride separated. After the action was complete the ethereal solution was shaken out with water and

then with sodium carbonate, dried over fused sodium sulphate, and the ether evaporated. There remained a thick syrup, which gradually deposited benzoic acid on standing *in vacuo*. The acid was filtered and the remaining liquid distilled under ordinary pressure. The result was identical with that observed with the thick oil obtained from sodium, aldehyde, and benzoyl chloride—*i. e.*, crotonic aldehyde, a liquid boiling between 75° and 90°, and some acetaldehyde[1] were obtained; benzoic acid, with a little aldehyde-resin, remained behind. There seems to be no doubt, therefore, that the second product of the reaction between benzoyl chloride, aldehyde, and sodium benzoate is aldol.

The reactions which have been given demonstrate that we have here, in all probability, a general method for preparing derivatives of substances, the sodium compounds of which are too easily decomposed to admit of isolation (as is the case with sodium aldehyde), for in this event the action of sodium on a mixture of benzoyl chloride and the body in question can be resorted to. It is strange that very little reduction of the aldehyde takes place during the action of sodium on the mixture; that this is the case, however, is shown by the fact that only a trace of benzoic ester was observed at any time during the progress of the work.

In conclusion, I wish to thank Mr. J. E. Whitsit for his ever willing assistance in this research.

ANN ARBOR, May, 1896.

II.—ON THE CONSTITUTION OF SOME DERIVATIVES OF FORMIC ACID.

BY PAUL C. FREER AND P. L. SHERMAN, JR.

FIRST PAPER.

Formic acid occupies a unique position in the series of homologous acids, of which it is the first member. It contains but one carbon atom in each molecule, and neither methyl nor methylene groups. Nevertheless, it has been customary to class it with the other members and to assume in it the existence of the carboxyl group—$C\overset{=O}{\underset{O-H}{\diagdown}}$. This struc-

[1] Acetaldehyde is always formed in small quantity from aldol on fractioning.

ture should give to the acid a dual character, and therefore the statement that formic acid is both an acid and an aldehyde is given in many of the text-books on organic chemistry.[1] Nevertheless, the aldehyde character is only expressed by the ease with which the acid is oxidized, for formates, either of the metals or of organic radicles, do not unite with bisulphites, nor does formic acid give the characteristic aldehyde reaction with fuchsine solution. Furthermore, formic acid acts upon phenylhydrazine to produce only the formate of the base, and finally by the separation of water, the hydrazide, but no compound which is analogous to the hydrazones, which can be produced from aldehydes, can be obtained directly from it. With ammonia the acid produces ammonium formate, and finally formamide, but here also the characteristic aldehyde ammonia reaction is lacking. The nearest homologue of formic acid which undoubtedly contains both an aldehyde and carboxyl group is glyoxylic acid, $CH(OH)_2$—COOH, and although the aldehyde group is hydrated, this substance most certainly conforms with other aldehydes in its entire behavior. In short it must be acknowledged that, if formic acid really does contain an aldehyde grouping, the latter most certainly lacks all of the characteristics, save one, of those bodies which we ordinarily regard as aldehydes.

Formic acid as a member of the homologous series of fatty acids should exhibit physical properties in conformity with those of its fellows, but nevertheless some of these are certainly at variance. So, for example, the difference between the boiling-points of formic and acetic acids is 17°; between acetic and propionic 23°; and this latter difference is pretty constantly observed in the case of the remaining members of the series. The transition of formic acid to acetic acid represents a replacement of hydrogen by methyl, so that for a more legitimate comparison it might be advisable to consider the difference between the boiling-points of propionic and isobutyric acids, and this is only 13°, as against 17° for that between formic and acetic acids. This abnormity in the boiling-points does not, however, show much as regards the

[1] Meyer and Jacobson: Lehrbuch der org. Chemie, I, 318: Beilstein, I, 394.

nature of formic acid, as methyl alcohol displays a similar variance from ethyl alcohol, while the halogen derivatives and amines show a decreasing difference for increasing atomic weights. The following table will show this relationship more clearly:

Name.	B. P. Degrees.	Diff. Degrees.	Name.	B. P. Degree.	Diff. Degree.	Name.	B. P. Degree.	Diff. Degree.
Hydroxylmethane	64.8		Chlormethane	—23.7		Brommethane	4.7	
Hydroxylethane	78.4	13.6	Chlorethane	12.5	36.2	Bromethane	38.4	33.7
Hydroxylpropane	97.4	19.0	Chlorpropane	46.4	33.9	Brompropane	70.8	32.4
Hydroxylbutane	116.8	19.4	Chlorbutane	77.9	31.5	Brombutane	100.4	29.6
Iodomethane	42.8		Aminomethane	—6.0		Methane acid	100.6	
Iodoethane	72.5	29.7	Aminoethane	18.7	24.7	Ethane acid	118.1	27.5
Iodopropane	102.2	29.7	Aminopropane	49.5	30.8	Propane acid	139.4	21.3
Iodobutane	131.4	29.2	Aminobutane	76.5	27.0	Butane acid	161.5	22.1

In some other physical properties also formic acid shows a variation from other members of the series. Thus its avidity is 1.68, as compared with 0.424 for acetic, 0.325 for propionic and 0.316 for butyric acid.[1] The difference between its magnetic molecular rotation and that for acetic acid is 0.854,[2] while the constant for the series is 1.010; although it must be remembered in this connection that the interval between acetic and propionic acids is also smaller than the normal (0.937). The difference in the heat of combustion between formic and acetic acids is 140[3], while the corresponding difference between acetic and propionic acid is slightly higher, being 156. Finally in its molecular refraction formic acid is entirely normal and conforms with its homologues. The above shows that, although a difference between formic acid and the others does exist in some respects, yet the study of the physical properties has thrown no light upon its construction.

If, however, formic acid is not both acid and aldehyde, as is generally understood to be the case, it then according to our present views of structural chemistry must be an unsaturated compound and be derived from a bivalent carbon atom $^{II}C<^{O-H}_{O-H}$. Such a formula at first glance seems extremely improbable, but a little consideration will show that

[1] Ostwald: Lehrbuch d. allg. chemie, **2**, 651.
[2] Ztschr. phys. Chem., **22**, 523.
[3] Ostwald: Lehrbuch d. allg. chemie, **2**, [1], 400-405.

it is not impossible. The acid would, if this structure were the correct one, be derived from carbon monoxide as an anhydride, and the ready formation of formates from carbon monoxide and alkaline hydroxides would favor this view. Furthermore, there is the marked tendency of formic acid to break down into carbon monoxide and water. Formic acid is monobasic, however, so that, even if it contains the two hydroxyl groups, only one of these is capable of forming salts, but this fact does not exclude the possibility of the hydroxyl formula, for just as tertiary sodium phosphate is so unstable as to be decomposed by water, and the tertiary phosphite does not exist at all, so might the secondary formate be an impossibility. It has been shown by Hell and Mühlhäuser[1] that formic acid can take up bromine in the presence of carbon bisulphide to form an unstable addition-product, which breaks down into carbon dioxide and hydrobromic acid, but, beyond this attempt to show the unsaturated nature of formic acid, nothing has been done. Hell and Mühlhäuser worked with a formic acid of 97 per cent. and claim that bromine and the acid do not unite except when carbon bisulphide is present, but this inactivity may easily have been caused by the impurities of the acid used.

A study of the literature of formic acid fails also to show any proofs of its ascribed aldehyde structure, except as has been mentioned, its well known reducing power.

The purpose of the present research is to throw some light on the constitution of the "formyl" group—CHO, both in the free acid and in combination. And with this object in view, we have first taken up the study of formylphenylhydrazine, formamide, and formic ether.

In the basic formyl derivatives[2] the formyl group is not reactive as an aldehyde. Formamide does not form the phenylhydrazone with phenylhydrazine, but, on the other hand, ammonia is separated and formylphenylhydrazine produced.[3]

[1] Ber. d. chem. Ges., 11, 245.

[2] The formates of both fatty and aromatic bases show a marked tendency to split off water and thus form the amides and hydrazides; in the case of phenylhydrazine, for example, this tendency is so marked that on pouring an excess of formic acid into phenylhydrazine, heat enough is generated to transform the formate into the hydrazide, $C_6H_5NH—NH—CHO$.

[3] Gazz. Chim., 16, 209.

The formation of formazyl hydrogen from formic ether, according to von Pechman,[1] if it were to be produced as that author thinks probable, by the action of a second molecule of phenylhydrazine on formylphenylhydrazine, $C_6H_5NH—NH—CHO + C_6H_5NH—NH_2 = C_6H_5NH—NH—CH = N—NH—C_6H_5 + H_2O$, and the further oxidation of the hydrazo- to the azo-group, would seem to contradict this statement, as this reaction indicates that the formyl group has an undoubted aldehyde character. On heating formylphenylhydrazine and phenylhydrazine together for several hours, even in the presence of zinc chloride, we found, however, that no reaction whatever had taken place, so that we were forced to conclude that this explanation is not correct. In regard to the formation of formazyl hydrogen, the conditions seem to be as follows: Formic ether when mixed with phenylhydrazine and kept cold and free from air, turns deep red and gradually deposits formylphenylhydrazine, while, at the same time, appreciable quantities of formazyl hydrogen are produced. The yield of the latter body is much increased if the temperature is raised, and of course that of formylphenylhydrazine is correspondingly diminished. On the other hand, if the free acid is brought into contact with phenylhydrazine, no formazyl hydrogen, or at least too small a quantity to be isolated, is produced in the cold, and this quantity is not increased perceptibly by heating. This would seem to indicate a difference between formic acid and formic ether, so that in the latter case the reaction would in part take place as follows:

$$C_6H_5NH—NH_2 + CHOOC_2H_5 = C\begin{matrix}H\\ \diagup\\ \diagdown\end{matrix}\begin{matrix}N—NHC_6H_5\\ OC_2H_5\end{matrix} + H_2O;$$

$$C\begin{matrix}H\\ \diagup\\ \diagdown\end{matrix}\begin{matrix}N—NH—C_6H_5\\ OC_2H_5\end{matrix} + H_2N—NH—C_6H_5 = C\begin{matrix}H\\ \diagdown\\ \diagup\end{matrix}\begin{matrix}N—NHC_6H_5\\ N=N—C_6H_5\end{matrix} + HOC_2H_5 + H_2.$$

This does not, however, indicate an aldehyde grouping in formic ether, for under the best conditions only a small part of the ether reacts in this way. It simply shows that the difficulty of saponifying formic ether gives an opportunity for a secondary reaction, which does not take place with the free

[1] Ber. d. chem. Ges., **25**, 3179.

acid. There is no proof therefore of the aldehyde structure of formic ether. The latter body readily reacts with sodium, as will be shown below, while orthoformic ether, which of course can have but one structure, does not react at all in the cold. The hydrogen attached to carbon, therefore, is not of an acid character, even where the strongly negative grouping $-C(OR)_2(OR)$ exists in close proximity.

The following structural formulas are, according to our present views, possible for the *basic* derivatives of formic acid:

I. $C(H)(=O)(NHX)$ II. $C(H)(OH)(NX)$ III. $C(=NH)(OH)(X)$

The only work which might have thrown light on this subject has been done with the metallic derivatives of these compounds. Hofmann,[1] whose work dates back to 1865, found that formanilide displayed the hitherto unknown property of forming a sodium salt, which although unstable, could nevertheless be isolated and analyzed. Tobias[2] extended Hofmann's results to ortho- and paraformtoluide, and prepared the sodium salts of these substances, and characterized them as easily crystallizing, colorless bodies, which, on standing, decompose into the corresponding bases and sodium formate. Norton and Livermore[3] found that sodium formanilide reacted with methyl iodide to form monomethyl formanilide and thus the synthetical value of the sodium salts of basic derivatives of formic acid was made apparent. To prepare the alkyl derivatives of aniline, Pictet and Crepieux[4] made use of the above outlined method for preparing the alkyl formanilides, and separated the formyl group by saponification with alkalies; while Harries[5] carried out the same reactions with phenylhydrazine, preparing in this way the di- and trialkyl derivatives. It will be observed that none of the above experimentation throws any light upon the constitution or behavior of

[1] Monatshefte d. Berl. Akad., 1865, 659.
[2] Ber. d. chem. Ges., **15**, 2450.
[3] *Ibid.*, **20**, 2273.
[4] Ber. d. chem. Ges., **21**, 1106.
[5] Ber. d. chem. Ges., **27**, 696.

the formyl group. Having in mind the well known property of silver salts to form oxyderivatives, Comstock and Kleeberg[1] treated sodium formanilide in alcoholic solution with silver nitrate. A silver salt was formed, which in its subsequent behavior with alkyl iodides differed materially from the sodium salt. For, when brought in contact with methyl iodide, silver iodide separated, and the resulting methyl derivative proved to be methyl isoformanilide, $C_6H_5N{=}CHOCH_3$. From this reaction Comstock and Kleeberg give to the silver salt the undoubtedly correct formula $C_6H_5N{=}CHOAg$. The free isoformanilide would, therefore, be represented by Formula II given above, and the methyl derivative an imidoether. In order that this supposition in regard to the constitution of the silver salt may be true, as well as that made in regard to the sodium salts, it must be taken for granted *a priori* that the alkyl group in every case assumes the place vacated by the metal. To see if this rule holds good in every case the study of formylphenylhydrazine was taken up, for with this compound exceptional conditions are offered.

When formylphenylhydrazine (1 mol.) is dissolved in a concentrated alcoholic solution of sodium ethylate (1 mol.), and the solution diluted with ether, a mono-sodium salt slowly crystallizes out on standing, which on exposure to the air turns red and breaks down into sodium bicarbonate and various basic compounds. To determine the position which the sodium holds in the molecule, the substance, both suspended in dry ether and in alcoholic solution, was subjected to the action of ethyl iodide. A reaction took place in both cases, but the resulting bodies showed marked differences, both in appearance and chemical behavior. In the first place a monoethylformylphenylhydrazine was obtained which melted at 106°, and crystallized in rhombohedrons. A study of its reduction-products proved it to have the following structure: $C_6H_5NH{-}N(C_2H_5)CHO$. The reaction product in the second case where the sodium salt of formyl-phenylhydrazine was dissolved in absolute alcohol, and an excess of ethyl iodide allowed to act upon it in the cold, was a monoethyl derivative having a melting-point of 78–79°, and crystallizing in

[1] This JOURNAL, 12, 492: 13, 255.

long needle-shaped crystals. Its constitution, as obtained through its reduction-products is, $C_6H_5N(C_2H_5)$—NH—CHO. We found that no traces of the other ethyl derivative were obtained until the reacting solution was heated at 100° under pressure for several hours, and even then the amount produced constituted but a small percentage of the entire ethyl compound formed. Under similar conditions free formylphenylhydrazine gave no ethyl derivatives whatever.

The above experiments would seem to show that one and the same sodium salt of formylphenylhydrazine is capable of forming two different, well-defined monoethyl derivatives, according to the conditions under which the reaction takes place. An explanation of this fact calls for something more than the theory of direct substitution of ethyl for sodium. Were that the only reaction possible between sodium formylphenylhydrazine and ethyl iodide, we should obtain but one ethyl derivative so long as there was but one sodium salt present. The fact that pure products were obtained under different conditions shows conclusively that the sodium salt could not have been a mixture, and its entire appearance and crystallographical properties support this view. This being the case the reaction must have taken place as follows: The possibility that the sodium atom is attached to oxygen is excluded, because were addition of ethyl iodide to take place at the unsaturated nitrogen-linking, with a subsequent splitting off of sodium iodide or hydriodic acid, we should obtain exclusively an ethyl derivative of the structure, C_6H_5—NH—N(C_2H_5)—CHO. But the fact that under certain conditions the body melting at 79° is the sole product of the reaction, shows that such an addition could not have taken place. For the same reason the structure, $C_6H_5NHN{=}C(OH).ONa$, is excluded. It follows from this that the sodium must be attached to one of the nitrogen atoms. One of these ethyl derivatives is then formed by direct replacement, the other by the addition of ethyl iodide to the neighboring nitrogen atom, this addition being then followed by separation of sodium iodide:

$$C_6H_5NH.NH.CHO + Na = C_6H_5.NH.NNa.CHO + H;$$

$$C_6H_5NH.NNa.CHO + C_2H_5I = C_6H_5.\underset{\displaystyle C_2H_5}{\overset{\displaystyle H\quad I}{N}}.NNa.CHO$$

$$= C_6H_5N(C_2H_5)NH.CHO + NaI.$$

The reason for such an addition to the sodium salt, where none takes place with the free body, is due to the increased positiveness of the nitrogen atom through the proximity of the sodium.

From the preceding experiments it will be seen that the position of the sodium atom cannot be stated with any degree of certainty, for the same reasoning would apply no matter to which nitrogen atom the sodium were attached. But it is to be presumed that addition takes place more readily in the cold than in the heat. Consequently the formula $C_6H_5NH.NNa.CHO$ is the more probable. The fact, however, that the ethyl derivative of the formula $C_6H_5NH—N(C_2H_5)CHO$, does not react with sodium ethylate nor sodium, shows that the sodium atom is attached to the nitrogen atom next to the formyl group.

The above results show that the position of a sodium atom cannot be determined from a study of the derived ethyl bodies. The result of Comstock and Kleeberg must therefore be interpreted as follows: In formanilide the proximity of the phenyl group renders the formyl group capable of reacting in its tautomeric or hydroxyl form, and, as a consequence, both the sodium and silver salts contain the metal attached to oxygen. The sodium, however, has a sufficient influence upon the nitrogen atom to render it capable of taking up methyl iodide so as to form the compound, $C_6H_5N=\overset{\displaystyle H}{\overset{|}{C}}—ONa$.

$$\underset{\displaystyle CH_3\quad I}{\overset{\displaystyle /\quad\backslash}{}}$$

Subsequently there is a separation of sodium iodide and the formation of the methyl formanilide $C_6H_5N(CH_3)—CHO$ or $C_6H_5\underset{\displaystyle \llcorner\!\!\!

takes place, but methyl is substituted directly for silver and the imido ether, $C_6H_9N=CHOCH_3$, is formed. With suitable alkyl or acyl halides and alteration of conditions, it will probably be possible to procure both oxy and nitrogen derivatives from the silver salt.[1]

In continuing the work on formyl derivatives we have performed a few introductory experiments with formamide. Auwers[2] has shown that bodies for which a hydroxyl grouping may be assumed in most cases display a peculiar cryoscopic behavior, in that the molecular weight rapidly increases with increasing concentration of the solution. This is notably the case with formamide. In order to see if the same results hold good for derivatives of formanilide, we repeated the work with the mono- and diethyl derivatives. Formanilide is insoluble in benzene, and ethylene bromide. Monoethyl formamide gave rapidly increasing molecular weights, while diethyl formamide remained constant. Thus, if Auwers' conclusions are correct, the monoethyl derivative contains a hydroxyl group. We prepared sodium formamide and found it to be a substance of exceptional stability when dry. It does not react with ethyl iodide even on heating to 130° under pressure. When moist it breaks down into ammonia and sodium bicarbonate.[3]

An unstable silver salt can be precipitated from aqueous solutions of sodium salt. Both the sodium and silver salts give back free formamide on decomposition with dilute acids. The action of sodium on monoethyl formamide is slow, accompanied by an evolution of hydrogen; with diethyl formamide no reaction takes place under twenty-four hours, and then decomposition, with the evolution of diethylamine, sets in.

[1] Since the above was written, Wheeler and Boltwood (This JOURNAL, **18**, 381,) have shown that the silver salt of formanilide gives *n*-acyl derivatives with benzoyl chloride.

[2] Ztschr. phys. Chem., **15**, 33.

[3] On treatment with bromine it apparently decomposes completely into sodium bromide, nitrogen and carbon dioxide, at least at present we have not been able to isolate anything else, and no addition-product could be identified. We intend to investigate this curious reaction further. The action of acetyl chloride on sodium formamide has given an oil which with alkalies readily breaks down into ammonia, acetic and formic acids. The results will be published in detail in a subsequent paper.

EXPERIMENTAL PART.

Formylphenylhydrazine, $C_6H_5NHNHCHO$.—To 200 grams of phenylhydrazine 200 grams of concentrated formic acid are added in one portion. Through the spontaneous generation of heat, the formate of the base which is at first formed, dissolves quickly, and after some hours standing, more quickly on cooling, the hydrazide crystallizes completely. After filtering and washing with ether and drying, the preparation is pure.

The very slight formation of formazyl hydrogen which accompanies the reaction is made apparent through the coloring of the liquid red, but not sufficient quantities of this substance were formed to be isolated.

Sodium Formylphenylhydrazine, $C_6H_5NHNNaCHO$.—In a glass-stoppered flask of some 250 cc. capacity, 10 grams of metallic sodium were dissolved in just enough absolute alcohol to form a clear solution. To this, when cold, were added 59 grams of powdered formylphenylhydrazine, and the flask tightly stoppered. The formylphenylhydrazine dissolved in sodium ethylate upon hard shaking, and a clear, slightly pinkish solution was formed. This solution was at once poured into a liter of ether, and allowed to stand in a cool place. Under these conditions no precipitation of sodium ethylate took place, while after a short time sodium formylphenylhydrazine began to crystallize in small bunches of felt-like needles. After twenty-four hours the crystallization was complete, and the salt was filtered, washed with ether and dried, care being taken that the entire process should be carried out in an atmosphere of dry hydrogen.

Sodium Determinations.

I. Some of the well washed sodium salt was dried quickly on a porous plate, transferred at once to a platinum crucible and weighed. The sodium was estimated as the sulphate.

II. A small amount of the salt was filtered into a Gooch platinum crucible, which was so fixed in a glass tube that the

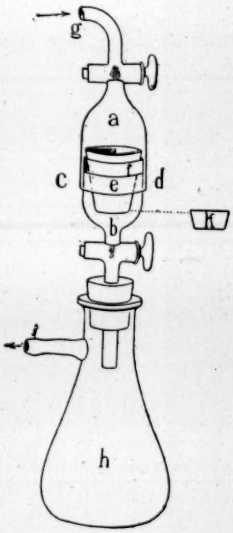
salt could be filtered and dried to constant weight in an atmosphere of hydrogen.[1]

	Calculated for $C_7H_7N_2ONa$.	Found. I.	II.
Na	14.55	14.40	14.23

The decomposition of the dry sodium formylphenylhydrazine in the air is very rapid. Aniline and phenylhydrazine are given off and sodium bicarbonate forms the principal part of the residue. When dissolved quickly in cold dilute hydrochloric acid, almost the theoretical amount of free formylphenylhydrazine may be recovered. A dry distillation of the body in an atmosphere of hydrogen gave aniline in large quantity.

Action of Ethyl Iodide on Formylphenylhydrazine.

To 2 grams of formylphenylhydrazine in a sealing-tube were added 2 grams of ethyl iodide and a small amount of absolute alcohol. The tube was sealed and allowed to stand over night. As no reaction took place, the tube was then heated for three hours at 100°. The solution on opening the tube was colored dark red. Both unchanged ethyl iodide and formylphenylhydrazine were recovered, also a small amount of dark colored decomposition-product. It is obvious, therefore,



[1] The accompanying cut will illustrate the apparatus used. *a* and *b* are tubes with a ground joint at *c d*, their other ends being closed by well-fitting, glass stop-cocks. The crucible *e* is held in place by the rubber band *f*. A small piece of filter paper is placed in the bottom of the crucible, the crucible put in place, and the entire apparatus, except the wash-bottle and cork, filled with hydrogen and weighed. The tube *a* is then removed, the substance quickly washed into the crucible with ether and the tube replaced. Dry hydrogen is allowed to enter at *g*, and is sucked out at *i*. After the substance has been dried to constant weight, the crucible is taken out, the cap *k* placed over the perforated bottom, and the sodium estimated in the usual manner.

that ethyl iodide does not react upon free formylphenylhydrazine under these conditions.

Action of Ethyl Iodide on Sodium Formylphenylhydrazine in Solution.

The reaction may be carried out by dissolving the freshly crystallized and dried sodium salt in absolute alcohol, and then subjecting it to the action of ethyl iodide. A quicker method, and one which gives exactly the same results, is the following: To the alcoholic solution of sodium formylphenylhydrazine, prepared as directed on page 572, care being taken to have the formylphenylhydrazine present in slight excess, somewhat more than the calculated amount of ethyl iodide was added, and the tightly-stoppered bottle allowed to stand 48 hours with occasional shaking. The reaction was finished when the mixture was neutral. The contents of the bottle were then poured into a distilling-flask, the alcohol and small amount of unchanged ethyl iodide boiled off under diminished pressure and at a low temperature and the oily remainder, together with the precipitated sodium iodide was poured into water. A heavy, colorless oil separated and solidified on standing. After drying on a porous plate and recrystallizing from ether, long, needle-shaped crystals were obtained, which melted without decomposition at 78–79°. These were easily soluble in all the organic solvents except petroleum ether. The following results were obtained on analysis:

	Calculated for $C_9H_{12}N_2O$.	Found.
C	65.85	65.69
H	7.31	7.43
N	17.07	17.31

The analyses give results agreeing with those of a monoethylformylphenylhydrazine. To determine the position of the ethyl group, 9 grams of the body were reduced in a boiling mixture of 8 grams of metallic sodium and 75 grams of amyl alcohol. The flask in which the reduction was carried out was so connected with an inverted condenser containing warm water, and with wash-bottles, that all gases and low-boiling products of reduction were carried over and absorbed by dilute hydrochloric acid. After the reduction was com-

pleted, and the metallic sodium entirely dissolved, the contents of the flask were poured into a separating-funnel, and shaken out with dilute hydrochloric acid, and the acid solution evaporated to dryness. A dark-colored, solid hydrochloride remained. This was decomposed with alkali, extracted with ether and distilled, boiling between 215–232°. The composition of one of the constituents of this oil, which was evidently a mixture, was easily determined by oxidation in ethereal solution with yellow mercuric oxide. Colorless prismatic crystals were precipitated from the solution. They melted at 108° and in other ways proved identical with Fischer's[1] phenylethyltetrazone $\begin{matrix} C_6H_5 \\ C_2H_5 \end{matrix} \diagdown N.N = N.N \diagup \begin{matrix} C_6H_5 \\ C_2H_5 \end{matrix}$. The oil must therefore be composed in part of *u*-ethylphenylhydrazine $C_6H_4N(C_2H_5).NH_2$. To determine the substance which was not acted on by the oxide, the etherial solution, from which the tetrazone had been filtered, was concentrated and the residue distilled with steam. A basic oil distilled over, and was easily identified as ethylaniline by means of its hydrochloride.

The contents of the wash-bottles, in which the gaseous reduction-products had been absorbed, were studied and found to contain nothing but ammonium chloride in small quantities. The products of the reduction were, therefore, unsymmetrical ethylphenylhydrazine, ethylaniline and ammonia. To have yielded these products, the constitution of the original body must have been $C_6H_4N(C_2H_5)NH—CHO$.

An attempt to ethylate *α*-ethylformylphenylhydrazine farther, by heating it for three hours at 100° under pressure with an excess of ethyl iodide, was without result, the body remaining unchanged.

Action of Ethyl Iodide and Sodium Ethylate on α-Ethylformylphenylhydrazine.

To a concentrated alcoholic solution of sodium ethylate containing 1 gram of metallic sodium, 7 grams of *α*-ethylformylphenylhydrazine and somewhat more than the calculated amount of ethyl iodide were added. The resulting clear

[1] Ann. Chem. (Liebig), 199, 327.

solution was heated under pressure at 100° for 30 minutes, when a large amount of sodium iodide had separated. After evaporating off the alcohol and unchanged ethyl iodide, the residue was thrown into water, and the heavy oil which separated, after washing with dilute acids and alkalies, was taken up with ether, the ether evaporated and the residue fractioned. On the second fractioning a pale yellow and rather light oil was obtained, which boiled regularly at 139–140° under a pressure of 5 mm. The analysis gave the following results :

	Calculated for $C_{11}H_{16}N_2O$.	Found.
N	14.58	14.93

The nitrogen determination gives figures corresponding to those of diethylformylphenylhydrazine. To determine the position of the ethyl groups, the body was reduced with sodium and amyl alcohol, following the method used in the reduction of the monoethyl body. The products of reduction were found to be ethylamine and ethylaniline. The former body was found as the hydrochloride in the hydrochloric acid wash-bottles, and was identified as such and also by means of the isonitrile reaction.

The further fact that alcoholic potash was incapable of breaking off an ethyl group even when warmed with it showed that no imido ether could be present. Diethylformylphenylhydrazine does not react with phenylhydrazine either at ordinary temperatures or when heated several hours under pressure. Further, the body does not react with sodium.

Action of Ethyl Iodide on Dry Sodium Formylphenylhydrazine.

Dry sodium formylphenylhydrazine, suspended in dry ether, was enclosed in a glass-stoppered bottle with an amount of ethyl iodide, slightly in excess of that required by theory, and heated for three hours at 100° in an autoclave. By this time the liquid was light red in color, and sodium iodide had been formed. The contents of the flask were treated with water, the ethereal solution separated, dried with calcium chloride, and distilled. The remaining solid product crystallized out of ether or alcohol in large rhombohedrons having a melting-point of 106°, and soluble in all the ordinary solvents except pe-

troleum ether and water. The yield is almost quantitative if sufficient care has been taken to free the sodium salt from alcohol. Otherwise varying amounts of the α-ethyl derivative will be formed, which will both decrease the yield and greatly increase the work of purification. The analyses gave the following results :

	Calculated for $C_9H_{12}N_2O$.	Found.
C	65.85	65.52
H	7.31	7.41
N	17.07	17.50

The results of the analyses show the body to be a monoethyl derivative of formylphenylhydrazine. As its melting-point and other physical properties easily distinguish it from the α-ethyl derivative, its constitution must be either (I) $C_6H_5NH—N(C_2H_5)—CHO$, or (II) $C_6H_5NH—N=CHOC_2H_5$. Its stability against saponification by either aqueous soda or alcoholic potash is evidence against the imido ether formula. A further proof of its constitution (I) is given by its reduction-products formed according to the previously described method. The bodies isolated were aniline and ethylamine. Several experiments were made to determine whether with ethyl iodide and an alcoholic solution of sodium formylphenylhydrazine any appreciable amount of the β-ethyl body was formed. Twenty-five per cent. of the entire quantity of the ethyl derivative formed was the largest yield, and this was obtained but once on heating the solution four hours at 100° under pressure. The average yield with varying temperature and duration of heating, as well as with different proportions of the reacting substances was only 5 to 7 per cent.

Action of Ethyl Iodide and Sodium Ethylate on β-Ethylformylphenylhydrazine.

The reaction was carried out in the same manner as described in the treatment of the α-ethyl body and afterwards also with a large excess of both ethyl iodide and sodium ethylate. The body remained entirely unchanged. Metallic sodium also did not react upon a xylene solution of the body when heated.

Action of Acetic Anhydride on Formylphenylhydrazine.

Formylphenylhydrazine (8 grams) were mixed with a slight excess of acetic anhydride. There was no reaction in the cold. Upon warming to 130°, there results a clear, thick syrup which does not crystallize. This syrup is perfectly soluble in water, soluble with great difficulty in moist ether, and insoluble in dry. On heating a mixture of formylphenylhydrazine and acetic anhydride in a distilling-flask, the reaction begins at 90° when acetic, but no formic, acid passes off. At 200° carbon monoxide is evolved, and when the pressure has been reduced to 35 mm. a thick oil distils, which partly solidifies on standing. The oily part is phenylisonitrile C_6H_5NC. The solid part was dried on a porous plate and recrystallized from benzene. Its melting-point, 126°, showed it to be symmetrical acetylphenylhydrazine. On treating the previously mentioned syrup with stannous chloride and tin, phenylhydrazine is formed. The body is, therefore, acetylformylphenylhydrazine, in which both the acid groups are attached to the same nitrogen atom. The acetyl group is, therefore, not attached to oxygen, and were formylphenylhydrazine a hydroxyl body, the result could only have been brought about by addition of acetic anhydride, and the subsequent splitting off of acetic acid. This supposition is not probable, however, in view of the fact that in sodium formylphenylhydrazine the sodium is attached to nitrogen. That the acetyl group is not attached to oxygen is also shown by the extreme difficulty with which acetylformylphenylhydrazine is decomposed by dilute cold caustic potash, months being necessary for its decomposition. The non-existence of oxyacetyl derivatives, however, does not absolutely prove the non-existence of a hydroxyl group.

Action of Benzoyl Chloride and Sodium Ethylate on Formylphenylhydrazine.

Metallic sodium (1.3 grams) was dissolved in absolute alcohol, and to the solution formylphenylhydrazine (8 grams) was added and mixed. On the addition of benzoyl chloride (8 grams) a reaction at once begins and is finished after two or three hours standing, when the odor of benzoyl chloride

has disappeared. A white solid slowly separates. After adding a small amount of soda and shaking well, the solid is filtered off and macerated with dilute caustic soda. After washing and drying, it may be recrystallized from alcohol. A small amount of the body can be recovered from the soda by acidifying. Its melting-point, 174–175°, and appearance characterize it as dibenzoylphenylhydrazine. From the alcoholic solution, containing the more soluble material, crystals separate. These melt at 134–141°, and when slowly recrystallized, they can be shown to consist of a mixture of mono- and dibenzoylphenylhydrazine, the mono-benzoyl body melting at 169°.

The only possible explanation of the above reaction is that hydrochloric acid was split off, and this in turn saponified the formyl group. This action of benzoyl chloride on sodium formylphenylhydrazine is exactly a counterpart of the reaction of ethyl iodide on the same body, only in the latter case as no free formylphenylhydrazine is formed, the separation of sodium iodide and not of hydriodic acid took place.

Sodium Dibenzoylphenylhydrazine.

Dibenzoylphenylhydrazine, when dissolved in concentrated sodium ethylate, gives upon standing and dilution with ether, a white, felt-like, crystalline sodium salt, from which an acetyl derivative can be prepared by boiling with acetyl chloride. The analysis gave the following result:

	Calculated for $C_{20}H_{15}N_2O_2Na$.	Found.
Na	6.81	7.01

Action of Chlorcarbonic Ether on Formanilide.

Wheeler having just published a paper[1] describing the action of chlorcarbonic ether on silver formanilide by which he obtained ethylisoformanilide and diphenylformamidine, it was of interest to discover if free formanilide would give the same results. The following experiment was therefore tried: To 10 grams of formanilide 9 grams of chlorcarbonic ether were added and warmed on the water-bath until solution took place and a slight evolution of carbon dioxide began. The liquid was then placed in a vacuum over lime until the odor

[1] This JOURNAL, 18, 381.

of chlorcarbonic ether had disappeared, and the evolution of carbon dioxide ceased. The oil was then washed with water until the aqueous solution upon neutralizing with alkali gave no precipitation. It was then free from halogen and could not be made to solidify upon cooling with a freezing-mixture. After standing a day, it was then transferred to a distilling-flask and placed in a vacuum, but after slight warming it broke down, giving off a gas and changing to diphenylformamidine, thus showing conclusively, according to Wheeler,[1] thai it was ethylisoformanilide, $C_6H_5N{=}CHOC_2H_5$.

On neutralizing with alkali, the water with which the oil was washed gave a white crystalline precipitate, which melted at 134–135°, and thus showed itself to be diphenylformamidine, $C_6H_5N{=}CH{-}\underset{H}{N}{-}C_6H_5$. The free formanilide therefore conforms to the silver salt in behavior.

Cryoscopic Molecular-Weight Determinations of Mono- and Diethylformamide.

Monoethylformamide.

Grams solvent (Benzene).	Grams substance.	Depression of freezing-point.	Concentration of solution. per cent.	Molecular weight found.
23.4823	0.0661	0.18°	0.28	76.6
"	0.1345	0.375	0.57	74.0
"	0.2807	0.635	1.2	93.0
"	0.4975	0.86	2.1	121.0

Diethylformamide.

23.2	0.0622	0.14°	0.27	96.0
"	0.2318	0.57	0.98	86.0
"	0.5098	1.01	2.20	97.0
14.6	0.7471	2.45	5.10	106.0

Sodium Formamide.

Five grams of sodium were dissolved in a slight excess of absolute alcohol, and the solution diluted with dry ether almost to precipitation of the sodium ethylate. To this solution 10 grams of pure formamide were added and well shaken. A crystalline precipitate forms at once. After a few hours' standing the precipitation is complete and the solution may be filtered, washed with alcohol and ether, and dried in a

[1] This JOURNAL, 18, 381.

vacuum over sulphuric acid. The analyses gave the following results:

	Calculated for H_2CONNa.	Found.
Na	34.32	33.42
N	20.89	20.91

Sodium formamide is stable when dry. On exposure to moist air, however, decomposition takes place, and ammonia is formed, together with sodium bicarbonate, and therefore these two decomposition-products in small amounts are always found in sodium formamide. When dissolved in cold, dilute hydrochloric acid, free formamide is regenerated. Investigations on the action of acyl chlorides and chlorcarbonic-ether on sodium formamide are in progress.

Silver Formamide.

Sodium formamide was dissolved in the smallest possible amount of ice-water, and to it was added the calculated amount of silver nitrate in concentrated aqueous solution. A silver-white, voluminous precipitate forms at once, which is very sensitive to light. When washed with alcohol and dried, it is a grayish powder, extremely soluble in water, and on decomposition with dilute acids, forms free formamide.

Action of Sodium on Formic Ether.

Pure formic ether was dissolved in absolute ether and subjected to the action of sodium in molecular proportions. The action was instantaneous, both hydrogen and carbon monoxide being given off, and in the proportion of one to two. An analysis of the remaining sodium compound proved it to be sodium ethylate. The reaction taking place may be represented as follows:

$$2HCOOC_2H_5 + 2Na = 2NaOCOC_2H_5 + H_2.$$

The sodium formic ether, which has but a momentary existence, then breaks down into sodium ethylate and carbon monoxide.

When amyl formate is substituted for the ethyl ether, the reaction is slower, and shows plainly the two phases mentioned

above. The gas at first given off in the reaction proved to contain 74 per cent. of hydrogen, while, towards the end of the reaction, only carbon monoxide was evolved. This would show that the sodium compound of amyl formate is capable of a short existence. When ethyl iodide is allowed to take part in the reaction, some traces of a body which colors ferric chloride may be obtained.

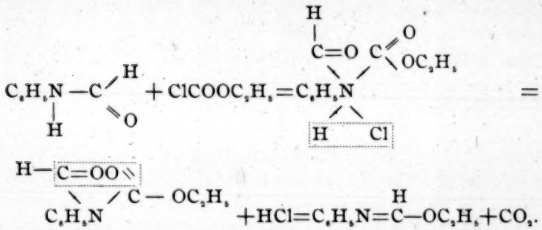
Sodium acting upon a mixture of ethyl formate and benzoyl chloride gave a brown sodium compound, apparently an addition-product, with a peculiar disagreeable odor. On standing, the body decomposed, giving off carbon monoxide, and leaving nothing but ethyl benzoate. Further investigations along this line will be undertaken.

Sodium in the presence of orthoformic ether was entirely indifferent.

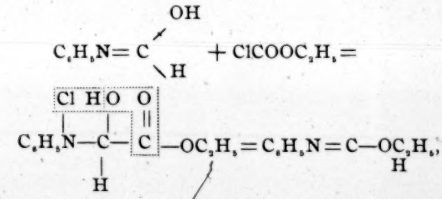
Summary.

The experiments show that in sodium formylphenylhydrazine the sodium is attached to nitrogen, and that, therefore, no hydroxyl group is present. They do not furnish any evidence of the presence of the aldehyde group, so that, at the present state of our knowledge, we must conclude that it has neither, and a structural formula according to our present theories is not possible.

In the salts, at least, of formanilide, there is strong evidence of a hydroxyl grouping. Regarding the free body, we can say nothing, for acetic anhydride reacts only to give an N-acetyl body, and chlorcarbonic ether, in forming ethylisoformanilide, may do so quite as well from the body $C_6H_5NH-C\begin{matrix}H\\O\end{matrix}$, as from the body $C_6H_5N=C\begin{matrix}H\\OH\end{matrix}$, for the ethoxy grouping may have its derivation from the chlorcarbonic ether as well as from the formyl group. The following equations will make this clear :



This splitting off of carbon dioxide and change of the hydrogen atom is parallel to that observed with dibasic acids on heating. It is certainly more readily comprehended than the other reaction:



in which the transference of ethoxyl must be assumed. In formanilide, therefore, it seems as if the free body were differently constituted from its salts.

The same may be said of free formic ethers, for they react with sodium, and in the case of amyl ether at least, there is a sodium compound produced which is capable of a brief existence. However, the reaction with zinc ethyl and zinc methyl to form secondary alcohols seems to point towards the grouping $C{=}O{<}^{H}_{OC_5H_{11}}$, so that the free ether is probably constituted according to that formula, while the sodium salt probably contains natroxyl. The decomposition of the sodium salt into sodium ethylate and carbon monoxide is much more readily understood if the latter formula, $C{<}^{ONa}_{OC_5H_{11}}$, is accepted.

It seems, therefore, that in order to react with sodium the hydrogen atom must be next to a carbonyl group or present as hydroxyl. However, it must be remembered in this connection that diethylformylphenylhydrazine, in which there is a grouping similar to that in formic ether, does not react with sodium, even on heating, so that these results are apparently contradictory, unless we believe that only in the case of the ethyl ether is tautomerism possible. It may be that in the action of sodium on formic ether, alcohol is separated and the reaction take place as it is supposed to do with acetic ether, but then there seems to be no reason why the ortho-ether should not act in the same way. The result shows, therefore, that different bodies, such as phenylhydrazine, aniline, or hydrogen, when attached to formyl have a different influence on the possibility of producing the natroxyl group. Why such a difference exists we cannot at present state.

III.—NOTES ON NEW APPARATUS.

1. THE ELECTROLYSIS OF HYDROCHLORIC ACID.

By Geo. O. Higley and B. J. Howard.

The electrolysis of hydrochloric acid in the lecture room, so as to show equal volumes of the two gases, has long been a vexatious subject for experimenters. The latest modification of the old Hofmann apparatus, suggested by Lothar Meyer,[1] is complicated and difficult to operate, while its results, at least in our hands, have not been accurate.

The simple apparatus which we have constructed, gives most satisfactory results. The accuracy of its operation depends upon the fact that the gases traverse but a small layer of liquid, while they are collected and measured in separate tubes, distinct from the ones which contain the eletrodes. They can also be measured under diminished pressure by the use of a leveling-bulb attached to the stop-cock *c* (Figs. 1 and 2.).

In order to operate the apparatus the small cups holding the electrodes are filled with a solution consisting of equal parts of concentrated hydrochloric acid and water, which has

[1] Ber. d. chem. Ges., 27, 850.

been saturated with chlorine, and to which an excess of sodium chloride has been added just previous to the experiment, the stop-cock *d* being kept open. The remainder of the apparatus is then filled with chlorine water, and all stop-cocks being closed, the current is turned on for five or ten minutes. The apparatus is then opened, the leveling-bulb adjusted so that the liquid rises to *d*, then *d* is closed, and electrolysis carried on under increased or diminished pressure. The results in the former case are less satisfactory than in the latter. With increased pressure from 8.5 to 9.3 cc. of chlorine are collected for every 10 cc. of hydrogen, while with diminished pressure the results are very nearly in absolute accord with theory. The gases are finally measured under atmospheric pressure.

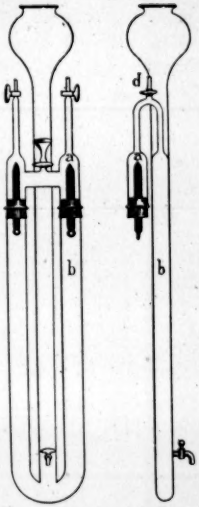


Fig. 1. Front view. Fig. 2. Side view.

2. DISTILLATION IN A VACUUM.

By P. C. Freer.

Distillation in a nearly absolute vacuum is now possible in every laboratory by the use of the Kahlbaum automatic mercury air-pump. One difficulty presents itself, where very low pressures are used, in the impossibility of obtaining tightly ground joints, so that more or less leakage has heretofore been unavoidable unless the expensive and complicated apparatus of Kahlbaum[1] is used. A simple receiver which answers the purpose admirably is shown in Fig. 3. *C* is a gutta-percha plug which is surrounded by a rubber ring, fitting tightly into a bell-mouthed cylinder, which is tubulated at the bottom of the widest part, and provided with a pinch-cock. The connection with the air-pump is made by *d*, and with the distilling-flask by *c*; *b* is a glass rod ground into a

[1] Ber. d. chem. Ges., **28**, 392.

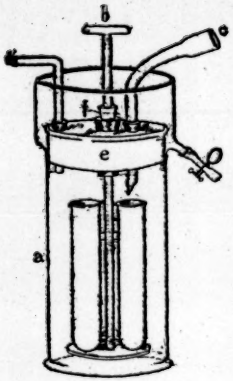


Fig. 3.

tube at *f* and carrying the receivers, the latter being fastened by rubber straps and a flat cork support below. The upper bell-mouth is filled with mercury after the apparatus is adjusted and before evacuating, so that a mercury valve is obtained for the entire receiver. The remaining joints for the thermometer and for the side tube in the distilling-flask can also be made into mercury valves by means of Kahlbaum's device. If desired, the tubulus of the distilling-flask can be bent so as to pass into the cap directly without an adapter and thus another joint be avoided. When distillation is over, the mercury is run off through the side tube in the cylinder. By the use of this apparatus and a Kahlbaum pump, vacua, which are practically perfect, can always be obtained without trouble.

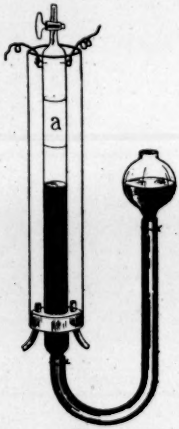


Fig. 4.

3. THE DEMONSTRATION THAT TWO VOLUMES OF HYDROGEN AND ONE VOLUME OF OXYGEN FORM TWO VOLUMES WATER VAPOR.

The apparatus of Hofmann is expensive and complicated, the explosion takes place under no very diminished pressure, and the eudiometer is often shattered. Besides, there is always an adjustment necessary after explosion so as to bring the mercury column back to its former height. The following modification is in my opinion a great improvement. It consists of a tube *a* (Fig. 4) with a stop-cock and platinum explosion-wires. The tube is jacketed and arranged so that it can be heated to 100°. The explosive mix-

ture is admitted by means of the stop-cock without any trouble, and measured under atmospheric pressure. The explosion is carried on under diminished pressure, so that any possible shattering of the tube is avoided, and finally by adjusting the leveling-bulb, the original conditions can quickly be reestablished.

ANN ARBOR, MAY, 1896.

IV.—THE ACTION OF METALS ON NITRIC ACID.

3. THE REDUCTION OF NITRIC ACID BY SILVER.

BY GEO. O. HIGLEY AND W. E. DAVIS.

In a former paper[1] it was shown that while the products of reduction of nitric acid by copper and lead are identical, *viz.*, —nitrogen dioxide, trioxide, nitric oxide and nitrous oxide— there is a striking difference in the respective proportions of these gases produced by the action of these two metals under the same conditions of temperature and excess and concentration of acid. Not only does lead produce nitrous oxide from a much greater variety of concentrations of acid, but also the metal-equivalent of this gas is about ten times greater than is obtained with copper under the same conditions. A similar difference appears throughout the whole work. It seemed, therefore, as far as the work had been carried, that each metal had a specific effect on the acid, and therefore that the action is probably one of direct deoxidation rather than of reduction through the medium of nascent hydrogen. In order to throw further light upon this point, a series of determinations have been made with silver, according to the method described in the previous papers upon this subject.

The metal employed was in the form of foil and was chemically pure. The quantity used in each experiment was 500 mg. In order to minimize the effect of reduction-products, the volume of acid was so chosen that there was present in every determination at least ten times the quantity of acid necessary for solution of the metal.

The results obtained are given in a table which shows: 1, temperature during solution; 2, volume and specific gravity of acids; 3, weight of nitrogen trioxide obtained from titration of nitrosyl-sulphuric acid contained in the Winkler tube;

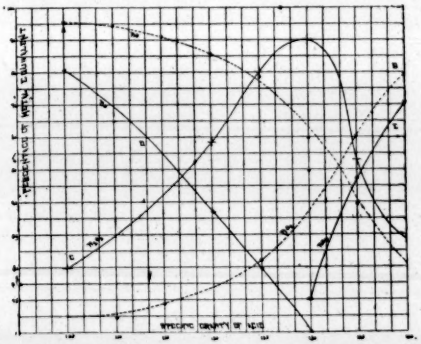
[1] This JOURNAL, 17, 18.

No. of experiment.	Temperature.	Acid. Volume.	Specific Gravity.	Winkler tube. Mgs. N_2O_5.	Nitrometer. Mgs. N_2O_5.	Nitric dioxide. Mgs.	Equivalent in Mgs. Ag.	Nitric trioxide. Mgs.	Equivalent in Mgs Ag.	Nitric oxide, cc.	Equivalent in Mgs. Ag.	Percentage Ag. found.
1	80°	50.0	1.05	17.44	....	....	....	17.44	98.88	27.75	401.65	100.1
2	80°	18.0	1.10	10.35	....	....	....	10.35	58.68	30.33	439.8	99.6
3	70°	18.0	1.10	30.2	....	....	....	30.2	171.2	22.36	325.0	99.25
4	60°	15.0	1.15	31.82	....	....	....	31.82	180.4	20.94	303.63	97.0
5	60°	15.0	1.15	21.97	....	....	....	21.97	124.79	24.68	357.86	97.0
6	20°	13.0	1.20	51.04	52.81	....	....	51.04	289.6	12.8	185.7	97.0
7	30°	12.0	1.25	69.75	68.18	....	....	69.75	392.4	6.5	94.3	97.6
8	30°	12.0	1.25	87.85	104.93	41.38	97.41	70.77	401.3	....	....	99.62
9	60°	11.5	1.30	88.66	115.67	65.34	149.12	61.65	349.55	....	....	99.7
10	60°	11.5	1.30	88.67	97.96	22.00	48.6	79.38	450.4	....	....	99.8
11	65°	11.0	1.35	87.85	129.75	101.13	232.19	45.8	267.0	....	....	99.1
12	65°	11.0	1.35	88.66	130.48	101.13	232.19	46.84	265.68	....	....	99.7
13	70°	10.0	1.40	88.67	147.82	134.57	332.00	29.6	167.0	....	....	99.7
14	70°	10.0	1.40	88.67	152.37	154.19	357.09	24.97	141.6	....	....	99.7

4, weight of trioxide obtained from nitrometer analysis; 5, weights of dioxide and trioxide of nitrogen with equivalent weight of metal; 6, volume of nitric oxide with weight of equivalent metal; 7, percentage of metal accounted for. The results are also given in the form of curves with specific gravity of acid as abscissæ and percentage of metal-equivalent as ordinates.

An examination of the table reveals the fact that the most concordant results are obtained with the stronger acids. In determinations made with acids having a specific gravity less than 1.30, the decomposition of nitrogen dioxide by water into nitric acid and nitric oxide seems to be, to some extent, independent of conditions.

Neither nitrogen nor nitrous oxide is produced by the ac-



tion of silver on nitric acid of any concentration with which work was done. This is in harmony with the results of Acworth and Armstrong,[1] who in three determinations made with silver and 1:2 acid, obtained only nitric oxide, the small amount of nitrogen collected being attributed to leakage of the apparatus. Montemartini[2] also states that as a result of the action of silver on 27.6 per cent. acid, only nitric oxide and nitrous acid are produced.

It now being definitely settled that nitrogen trioxide does

[1] J. Chem. Soc., 33, 71. [2] Gaz. chim. ital., 22, 405.

not exist in the gaseous condition,[1] curves *C*, *D*, and *E* are given principally for purposes of comparison with those previously published.

Curves *A* and *B* are obtained by adding to the metal equivalents of nitric oxide and nitrogen dioxide respectively, the amounts obtained by calculating nitrogen trioxide into nitric oxide and dioxide and then into metal.

Nitrogen dioxide is the principal reduction-product with concentrated acid, accounting for over 70 per cent. of the metal dissolved. In experiments with acids of greater degrees of dilution there is a rapid and somewhat regular decrease of this gas due to a greater tendency to decomposition with water into nitric oxide and nitric acid.

Curve *A*, that of nitric oxide, is the complement of that of the dioxide since it represents the decomposition-product of the latter.

Silver is less reactive than copper, since the latter, when dissolved in dilute nitric acid (sp. gr. 1.05–1.15), yields nitrous oxide, accounting for from five to fifteen per cent. of the metal employed, while the former produces no nitrous oxide under the same conditions.

V. — ON THE ESTERIFICATION OF HALOGEN-SUBSTITUTED ACETIC ACIDS.

SECOND PAPER.

By D. M. Lichty.

A preliminary investigation of the esterification of the chloracetic acids by ethyl alcohol, reported by me to this Journal,[2] showed the desirability of conducting research in this direction, at a lower temperature than 154° (adopted at that time for the sake of making the results comparable with those of Menschutkin), and of making the initial period, for which the amount of etherification is determined, as short as possible.[3] The reasons for this alteration were two-fold: First, decomposition, to a greater or lesser extent, takes place with halogen-substituted acetic acids at the higher temperature (154°), while I have convinced myself that at 80° none is

[1] Lunge and Porschnew: Ztschr. anorg. Chem., 7, 209

[2] Vol. 17, 27.

[3] *Ibid.*, 31.

observed, unless the period during which the heating continues is long.[1] Since, as will be shown by the data recorded in this paper, the influence of the halogens is very pronounced during the initial stages of esterification and comparatively small in the final, and since therefore, this decomposition toward the end of long periods is of no great moment, the latter temperature was selected for the thermostat. Secondly, short intervals for the determinations would enable me to construct a velocity-curve for the reactions which would give me a complete insight into the results, a thing not to be obtained if the first determination is made after one hour, after the method of Menschutkin. The alterations in the conditions have given most satisfactory results, and the curves demonstrate that the rate of esterification depends on two factors, one the mass-action of water *versus* alcohol, and the other the specific nature of the acid. The experimental part contains the results obtained with mono-, di- and trichloracetic acids.

Chloracetic Acids and Ethyl Alcohol.

The method used in these determinations is essentially identical with that reported in the previous paper, the only departures being those mentioned in the introduction. These consisted

(1) In selecting 80° as more suitable than 154°, secondary reactions being wholly absent at the former temperature, while at 100° and above there is more or less decomposition, as is shown by the development of gas or by carbonization.[2]

(2) In beginning the estimations at the end of one minute instead of one hour.

(3) In sealing into the tube with the alcohol and acid a piece of glass rod which served to break the alcohol bulb

[1] This was observed with tribromacetic acid.

[2] A mixture of equivalent quantities of monochloracetic acid and alcohol, heated for several days in a sealed tube at 154°, yields chloracetic ester, glycolic ester, ethyl chloride in large quantities, glycolic acid and glycolides. The reaction is such as to make the degree of esterification finally reached, much less than it is at the end of an hour. This falling off is obviously due to the decomposition of the ester, and the formation of these secondary products. In the case of trichloracetic acid, the action of the water formed by the esterification probably changes the acid to chloroform and carbon dioxide, a reaction which is well known, and which would soon decrease the amount of free acid present, just as experiment shows to be the case.

after the tube and its contents had reached the temperature of the glycerin-bath, thus making it possible to have the temperature the same during the entire period of reaction, an important condition for the attainment of accurate results for the short interval determinations. The esterification was stopped by immersing the tubes in water at about 15° C., and the free acid remaining was determined by means of ammonia, approximately decinormal, with rosolic acid as indicator.

Monochloracetic Acid and Ethyl Alcohol.[1]

Time (Minutes).	Percentage of acid converted.					Mean.
1	1.6	1.67	1.72	1.83	2.07	1.78
3	5.10	5.15	5.08	5.06		5.09
5	8.34	7.50	6.77	6.99		7.65
10	12.34	12.87	13.19	14.24	14.27	13.38
15	18.25	19.62	18.18	16.57		18.15
20	22.82	23.51	22.09	20.91		22.23
25	25.09	27.54	25.07	26.05	25.83	25.91
30	28.35	28.85	28.66	28.67		28.63
45	35.59	35.75	36.16	36.36		35.96

Time (Hours).	Percentages.		Mean.
1	41.63	42.10	41.89
2	57.55	57.11	57.33
3	61.80	60.98	61.39
5	62.15	63.15	62.65
10	66.97	67.29	67.13
14½	67.48	67.42	67.45
24	67.48		67.48
42	66.41	69.23	67.82
48	68.03	68.02	68.12
157	68.68	68.62	68.65

Discussion of Data.—The initial rate of esterification is 1.78 per cent. During the first three minutes 5.09 per cent. of the acid is esterified, or 1.69 per cent. per minute; during the first five minutes 7.65 per cent., or 1.53 per cent. per minute. The rate continues to decrease as the time increases, and somewhere between 20 and 25 minutes it is numerically equal to the time in minutes. From this point the mean increment in percentage of acid esterified is less than one unit for each increment of one minute in time, becoming about two-thirds of a unit for a period of one hour; less than half a unit for a period of two hours, and but little more than one-third of a unit for

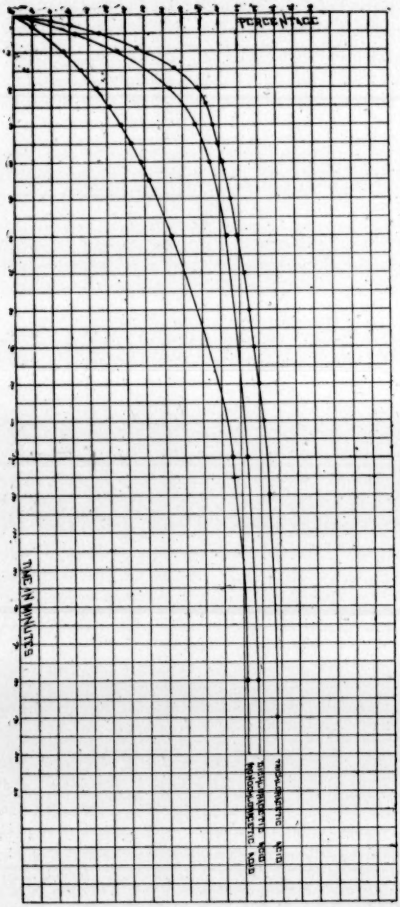
[1] One molecule of each.

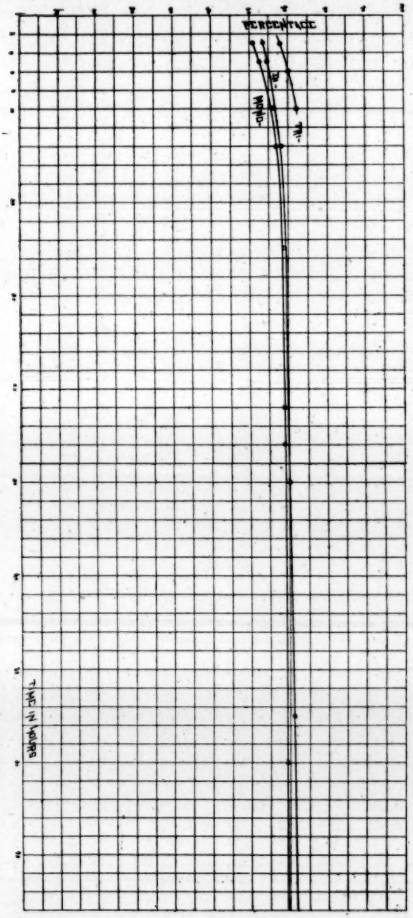
three hours. After this the esterification proceeds very slowly, reaching at the end of 24 hours a value about one unit below that obtained at the end of 157 hours, when the amount esterified is 68.65 per cent. The decrease in the rapidity of esterification is thus seen to be gradual, but quite regular. This is shown very clearly by means of the curve plotted by taking the time (in minutes) as abscissæ, and the percentages as ordinates. (See accompanying plates.) In general, the lack of concordance in the results obtained in several cases at the end of the same interval in different trials, during which the conditions were apparently the same, shows clearly that the course of the process is influenced by conditions which are not readily detected, and which are therefore very difficult to control.

Since the limit to which the esterification of a given acid and a given alcohol, mixed always in the same proportions, may be carried, is independent of the temperature[1] and of small differences in the sizes of the tubes,[2] its value for one acid and a given alcohol, at one temperature, may properly be compared with that for another acid and the same alcohol at another temperature, provided that the tubes in which the reactions take place do not differ much in size. Since the latter condition was fulfilled, we shall compare the limits obtained with acetic and monochloracetic acids respectively, and we find that they differ by about two units, being 66.57 per cent. for the former and 68.65 per cent. for the latter. The substitution of one atom of chlorine for hydrogen in acetic acid has then only a slight influence upon the limit of esterification.

The rate of esterification depending upon the temperature, it is not legitimate to compare the rate for the acid under consideration, obtained at 80°, with that for acetic acid, until the esterification of the latter is also investigated at the same temperature. The amount of each acid which is esterified in one hour at 154°, has been determined, the hour rate for acetic acid being 46.95 per cent. (Menschutkin[3]), and for monochloracetic acid 67.01 per cent.[4] The rate for the latter acid exceeds that of the former by 20 units, or about 43 per cent.

[1] Berthelot and Péan de Saint Gilles: Ann. chim. phys. [3], **68**, 234–238, (1863).
[2] *Ibid.*, **68**, 239–245. [3] Ber. d. chem. Ges., **11**, 1507; Ann. chim. phys. [5], **20**, 305.
[4] This JOURNAL, **17**, 29.


PERCENTAGE
TIME IN MINUTES
TRICHLORACETIC ACID
SULPHOSALICYLIC ACID
PHOSPHOTUNGSTIC ACID


PERCENTAGE
TIME IN HOURS

Esterification of Dichloracetic Acid and Alcohol.[1]

Time.	1m.	3.	5.	10.	15.	20.	30.	40.	1h.	2.	3.	5.	10.	20.	25.	50.	75.	100.	
Percentage.	5.83	10.09	19.87	30.60	37.17	43.73	47.62	51.79	56.87	60.94	60.08	65.28	66.19	67.73	67.94	70.34	69.10	71.42	74.07
	3.48	11.00	19.57	26.17	34.35	44.96	47.76		58.50	58.79	59.88	64.46	66.53		68.92	67.08	69.30	71.02	67.86
	5.61	11.70	17.16	32.71	34.27	46.62	49.64		57.34	58.60	68.34	63.43	67.87			67.36	69.20	70.51	69.07
	4.27	13.54	12.36	32.85	40.49	40.96	46.74		57.31	65.10	67.26	66.00					74.10	70.84	74.89
	4.08	10.31	12.57	29.30	35.46	40.08			57.07	65.80									
	4.10		17.36	28.31		39.75			55.75	64.84									
			16.52	25.12					54.55										
			16.35	24.70					54.43										
				23.95					56.55										
Mean.	4.56	11.33	16.48	28.08	35.53	42.68	47.94	51.79	56.49	62.34	63.88	64.95	66.84	67.73	68.43	68.29	70.42	70.95	71.22

[1] One molecule of each.

Could a comparison be made between minute rates the percentage increase in the rate due to the substitution of one atom of chlorine would without doubt be much higher than the above.

Discussion of Data.—An inspection of the mean values in the foregoing table shows that the initial rate of esterification of dichloractic acid and ordinary alcohol is 4.56 per cent., which is 2.56 times the initial rate for monochloacetic acid; that the mean amount of acid esterified during the first three minutes is 11.33 per cent., or 3.77 per cent. per minute, and that the amount esterified during the first five minutes reaches 16.48 per cent., or 3.3 per cent. per minute. The reaction at first subsides a little more gradually than in the case of monochloracetic acid, but from the end of the twenty-minute period more rapidly. (See curve.) The mean increment becomes at the end of the first hour nearly one unit per minute, numerical equality between the time in minutes and the per cent. esterified being reached some minutes before the end of the first hour. For the first two hours the mean increment is about one-half of a unit per minute; for the first three hours a little over one-third of a unit per minute. The mean of four determinations of the limit of esterification is 71.22 per cent., which is less than three units above the limit for monochloracetic acid.

Trichloracetic Acid and Ethyl Alcohol.[1]

Time.	1m.	2.	3.	4.	5.	7.	9.
Percentages.	10.29	15.78	18.49	22.17	23.32	28.41	32.68
	9.70	15.02	19.36	22.89	23.28	27.67	31.91
				22.91	23.15		
				22.43	23.21		
Mean	9.99	15.40	18.92	22.60	23.24	28.04	32.30
Time.	11.	13.	15.	17.	20.	23.	26.
Percentages.	36.83	39.84	43.16	45.84	49.15	50.18	52.16
	36.08	39.57	42.81	45.98	48.91	50.74	51.51
Mean	36.45	39.70	42.98	45.91	49.03	50.46	51.83
Time.	30.	35.	40.	50.	60.	70.	80.
Percentages.	53.19	54.44	55.79	57.49	59.42	61.35	62.26
	52.86	54.32	55.23	57.23	59.23	60.82	62.34
Mean	53.02	54.38	55.51	57.36	59.39	61.08	62.30

[1] One molecule of each.

Time.	90.	100.	110.	120.	130.	160.	190.
Percentages.	63.71	64.29	65.32	66.24	67.17	67.42	68.36
	63.39	64.37	65.56	66.13	66.64	67.66	68.15
Mean	63.55	64.33	65.44	66.18	66.90	67.54	68.25

Time.	4h.	6.	10.
Percentages.	68.41	70.15	72.26
	68.52	70.02	72.41
Mean	68.46	70.08	72.23

Discussion of Data.—For this acid the initial rate is 9.99 per cent., which is 5.61 times the rate for monochloracetic acid, and 2.19 times that for dichloracetic acid. During the first three minutes the amount of acid esterified reaches 18.92 per cent., a mean rate of 6.31 per cent. per minute, while at the end of the first five minutes the amount esterified is 23.24 per cent., a mean rate of 4.65 per cent. per minute. Numerical equality between the time in minutes and the percentage esterified is reached between one hour and one hour and ten minutes. The mean increment becomes about half a unit per minute at the end of two hours and ten minutes, and about one third of a unit at the end of three hours. There is therefore great similarity between the courses taken by the esterification of di- and trichloracetic acids respectively. This fact is still more plainly shown by the graphic representation of the reactions.

The amount esterified at the end of ten hours was found to be 72.33 per cent., and since this value is but two units above that for a period of six hours, it cannot be far from the limit, which therefore is only a few units higher than that of dichloracetic acid.

Summary.	Mono-.	Di-.	Tri-.
Initial rate,	1.78	4.56	9.99
Mean rate duting first 3 minutes,	1.69	3.77	6.31
" " " " 5 "	1.53	3.30	4.65
Time at end of which there is numerical equality between number of minutes and percentage,	Between 20 & 25	Between 50 & 60	Between 60 & 70

Summary.	Mono-.	Di-.	Tri-.
Time elapsed when the mean increment in percentage per minute is one-half of a unit,	About 110 m	About 130	About 130
Time elapsed when the mean increment in percentage per minute is one-third of a unit,	A little over 3 h	Between 3 and 4h	About 3h 10m
Limit,	68.65	71.22	About 74.00

The limit of esterification of acetic acid is 66.57 per cent. The substitution of chlorine for hydrogen in acetic acid increases the limit of esterification by 2.08 units, or 3.1 per cent. over 66.57 for one atom of chlorine; by 4.65 units, or nearly 7 per cent. for two atoms, and possibly by 7.5 units, or nearly 11.5 per cent. for three atoms. On the other hand, the initial rate of dichloracetic acid is 2.56 times that of monochloracetic acid, an increase of 156 per cent.; while the initial rate of trichloracetic acid is 5.61 times that of monochloracetic, an increase of 461 per cent. The influence of chlorine is therefore very much greater upon the rate of esterification than upon the limit.

An examination of the curves plotted by taking the time in minutes as abscissæ and the percentages as ordinates shows that those for tri- and dichloracetic acids, respectively, have nearly the same slope, being very steep for the first 20 minutes, and then rapidly turning away from the axis of ordinates toward parallelism with the axis of abscissæ. The curve for monochloracetic acid has at first a slope which is entirely different from that for the other two, lying about midway between the two axes between ten and fifteen minutes; *i. e.*, making with each an angle of 45°. At twenty minutes the angle with the axis of abscissæ is perceptibly smaller than that with the other axis, and the curve continues from this point to turn gradually towards parallelism to the axis of abscissæ. Beyond three hours the three curves are nearly parallel to each other. It seems probable that the mathematical equations for these are very different, but I shall not attempt to derive any mathematical expressions until more data have been obtained by investigating other halogen-substituted acids in the same manner.

This research will be next extended to acetic acid, the bromacetic acids and the halogen propionic acids; to the first to enable us to determine more completely the influence of the halogens upon the initial rate of esterification; to the second to learn whether the courses of the esterification of these acids are similar to those of the corresponding chlorine compounds and what relation exists between the influence of the two halogens; to the third to discover the influence of the position of the halogen.

The author wishes to take this opportunity to thank Mr. S. R. Cook and Mr. Firman Thompson for valuable assistance in this work.

VI.—THE CONSTITUTION OF THE ACID AMIDES.

By Arthur Lachman.

It is only during the last few years that doubts have arisen as to the correctness of the commonly accepted acid amide formula. In 1890 Tafel and Enoch[1] showed that when ethyl iodide acted on benzamide silver, benzimidoethyl ether was obtained; and as they could not isolate any other compound excepting benzamide from the silver salt, they concluded that possibly benzamide was constituted according to the tautomeric hydroxy formula $C_6H_5C\begin{matrix}//NH\\\backslash OH\end{matrix}$. Two years later, Pinner[2] found that benzimido acetate, $C_6H_5C\begin{matrix}//NH\\\backslash O.COCH_3\end{matrix}$, is identical with acetyl benzamide, $C_6H_5CONH.COCH_3$; he did not attempt to show which of the structures in question really characterized the substance. Auwers,[3] during a series of molecular-weight determinations in benzene solution, discovered that a number of amides behaved cryoscopically as if they contained hydroxyl groups. And lastly, Cohen[4] has attempted to prove the hydroxy formula by showing, on the one hand, that some amides add sodium ethylate, and, on the other, that the fact that certain amides do not form silver salts may be explained upon a *stereochemical* basis, if we adopt the formula he advocates.

None of this work, however, can be said to have in any way

[1] Ber. d. chem. Ges., **23**, 103. [2] *Ibid.*, **25**, 1435.
[3] Ztschr. phys. Chem., **12**, 644; **15**, 33.
[4] Brit. Assoc. Reports, 1894, 625; J. Chem. Soc., **69**, 19.

contributed to a definite solution of the problem of the amide configuration. We now know that salts may have a different structure from their mother substances—*e. g.*, acetoacetic ether and its salts,—and that an entering alkyl group does not take the place of the metal atom which leaves the molecule. Pinner's result has no special significance until it is shown that benzimido acetate does or does not suffer a rearrangement of its atoms during the process of formation. The results of the cryoscopic investigation are by no means binding, as Auwers himself takes care to emphasize. And as to Cohen's work, the addition of sodium ethylate has as little to do with the hydroxy formula as the absence or presence of silver salts suffices to establish a geometric isomerism. The evidence for the hydroxy formula is rather weak, therefore, as far as the work is concerned that is supposed to establish it.

Previous to a more detailed study of the literature of the subject, however, I am totally unprepared to find that there was scarcely better reason for clinging to the ordinary formula ; in fact, the newer had somewhat the advantage.

This assertion is easily substantiated. First of all, it will be best to discuss methods of formation. Manifestly, methods of formation cannot be drawn into the argument, because we judge the steps of a reaction by the resulting products ; the *reaction itself* escapes our ken, and is merely an *ex post facto* deduction. Therefore the analogy of formation of, *e. g.*, acetamide and dimethylacetamide is valueless, for with acetamide the reaction may possibly have gone a step farther :

$$CH_3COCl \rightarrow CH_3CON(CH_3)_2 ; \quad CH_3COCl \rightarrow CH_3CONH_2 \rightarrow CH_3C\begin{matrix}\diagup\!\!\diagup NH\\ \diagdown OH\end{matrix}.$$

The *chemical* analogy of acetamide and dimethyl acetamide is at present an unproved assumption.

And so we may rule out the following cases :

1. Amidoximes,[1] on warming with water, give amines and hydroxylamine :

$$CH_3C\begin{matrix}\diagup\!\!\diagup NOH\\ \diagdown NH_2\end{matrix} + H_2O = CH_3C\begin{matrix}\diagup\!\!\diagup O\\ \diagdown NH_2\end{matrix} + H_2NOH.$$

[1] C. F. Nordmann : Ber. d. chem. Ges., 17, 2746.

2. Imidoether hydrochlorates[1] when heated, yield amides and alkyl chlorides:

$$CH_3CCl\begin{matrix}\diagup NH_2\\ \diagdown OC_2H_5\end{matrix} = CH_3C\begin{matrix}\diagup NH_2\\ \diagdown O\end{matrix} + C_2H_5Cl.$$

3. Nitriles and water yield amides[2] in exactly the manner in which nitriles and alcohols yield imidoethers:

$$CH_3.CN+HOH=CH_3C\begin{matrix}\diagup NH\\ \diagdown OH\end{matrix};\quad CH_3.CN+C_2H_5OH=$$

$$CH_3.C\begin{matrix}\diagup NH\\ \diagdown OC_2H_5\end{matrix}.$$

It will be noticed that a rigid interpretation of these reactions would lead to contradictory results, as *two* point to the old, and *one* to the new formula.

On examining the *reactions* of the amides, one fact stands out prominently, *viz.: that the amides differ widely in behavior and that they cannot be considered as one group of compounds.* On the contrary they seem to fall into *two* classes, and the behavior of these two classes *is on the whole what would be expected of compounds having the normal amide structure on the one hand, and the imido hydroxy structure on the other.*

Behavior of the Amides Towards Reagents.

All the amides seem to form condensation-products with aldehydes. In these condensations the amides all react like *secondary* bases; one molecule of aldehyde unites with two of amide. But as some of the amides which condense as secondary bases behave in every other respect as normal amides, this reaction cannot be used in favor of the imide formula. The structure of these condensation-products has been deduced from that of the amides, and as heretofore the latter have all been formulated alike, the condensation-products have been uniformly represented as follows:

$$R.CH<\begin{matrix}NH.CO.R.\\ NH.CO.R.\end{matrix}$$

The action of hydroxylamine on amides has been examined only in a fragmentary manner. According to Janny,[3]

[1] Pimer and Klein: *Ibid.*, 10, 1892: Lengfeld and Stieglitz: This JOURNAL, 17, 105.
[2] Pinner and Klein: Ber. d. chem. Ges., 10, 1896.
[3] Ber. d. chem. Ges., 15, 2783.

urea does not react. C. Hoffman[1] has shown that both acetamide and benzamide are acted upon, yielding, however, not amidoximes, as would be expected of normal amides,

$$R.C\begin{matrix}=O\\ \diagdown NH_2\end{matrix} + \begin{matrix}H_2\\ \diagup NOH\end{matrix} = H_2O + R.C\begin{matrix}\diagup NOH\\ \diagdown NH_2\end{matrix};$$

but hydroxamic acids, as might be expected of imido acids:

$$R.C\begin{matrix}=NH\\ \diagdown OH\end{matrix} + \begin{matrix}H_2\\ \diagup NOH\end{matrix} = NH_3 + R.C\begin{matrix}\diagup NOH\\ \diagdown OH\end{matrix}.$$

The indifference of the amides toward nitrous acid does not rest upon any detailed investigation. As far as it goes, it is best interpreted by the imido formula; the absence of nitroso derivatives might be brought under Baeyer's[2] rule, that imides are the more indifferent to nitrous acid, the less basic the molecule.

Nitric acid, under proper conditions, converts some amides into nitramides (benzene sulfonamide,[3] urea,[4] urethane, guanidine,[5] dicyandiamide[6] and biuret); whereas acetamide[7] and benzamide are decomposed. The formation of primary nitramides would require the amide formula

$$R.CONH_2 + HONO_2 = R.CONH.NO_2 + H_2O,$$

and the amides which are decomposed by nitric acid probably have some other structure.

The action of phosphorus pentachloride on amines was made the subject of a very extensive investigation by Wallach.[8] Wallach concluded that in *all cases* the oxygen atom is first substituted by two chlorine atoms, thus:

$$R.CONH_2 + PCl_5 = R.CCl_2NH_2 + POCl_3,$$

forming amide chlorides, and that these amide chlorides then lose hydrochloric acid, forming imide chlorides, nitriles, or certain complicated bases. The fact that amide chlorides, even under the most favorable conditions, were extremely un-

[1] *Ibid.*, **22**, 1854.
[2] *Ibid.*, **21**, 682.
[3] Hinsberg: *Ibid.*, **25**, 1195.
[4] Ann. Chem. (Liebig), **288**, 266.
[5] *Ibid.*, **270**, 1.
[6] Ber. d. chem. Gss., **27**, 1520.
[7] Rec. trav. chim., **2**, 95.
[8] Ann. Chem. (Liebig), **184**, 1; **214**, 193.

stable substances, lent color to the general applicability of this interpretation. But a closer examination of Wallach's results leads to a somewhat different interpretation. Only in *one case*—oxamethane—was Wallach able to isolate the amide chloride of an unsubstituted amide. Actamide, mono-, di-, trichloracetamide and benzamide, on treatment with pentachloride gives off hydrochloric acid *immediately*. The unbiassed consideration of these results led to the conclusion that oxamethane *really has the amide formula*, whereas acetamide, benzamide, etc., react *as if they contain hydroxyl groups*.

The action of acid anhydrides and chlorides has been investigated on many sides. Acetic anhydride, for instance, seems to react with all amides alike; acetamide[1] yields diacetamide, benzamide,[2] acetyl benzamide, urethane,[3] acetyl urethane, etc. Acetyl chloride, however, is selective in its action. Acetamide and benzamide[4] do not form acetyl derivatives with it, but suffer the loss of water in part; the same is true of the action of benzoyl chloride[5] on these amides. On the other hand, urea, urethane, oxamethane, are more or less readily converted into acetyl or benzoyl bodies by the corresponding chlorides. Thus we find here the same *difference* in behavior between certain groups of amides referred to above; those amides whose other properties render it probable that they contain the normal $CONH_2$ group giving the normal amine reaction with acid chlorides; the other amides behaving abnormally, though for no evident reason. This difference between the amides is not due to the greater basicity of those which form derivatives with acid residues; for urethane is much less basic than benzamide, and oxamethane has no basic properties whatsoever.

An exception to this grouping of the amides seems to occur when carbonyl chloride is employed. E. Schmidt[6] obtained from this reagent and acetamide a substance which has the composition of diacetylurea, and from benzamide the corresponding compound. But these substances are not the main products of the reaction at any time, being in fact formed only

[1] Heutschel: Ber. d. chem. Ges., **23**, 2395.
[2] Pinner: *Ibid.*, **25**, 1435.
[3] M'Creath: *Ibid.*, **8**, 1182.
[4] Pinner: *Loc. cit.*
[5] Pictet: Ber. d. chem. Ges., **23**, 3015.
[6] J. prakt. chem. [2], **8**, 63.

at high temperatures; in the cold not a trace of these compounds is formed; and the conclusion is evident that these diacylureas result from the interaction of the primary products. In addition, Schmidt's compounds have properties decidedly at variance with those of other acylated ureas. Thus, they are insoluble in alkalies; on warming the mixture, they break down into amides and carbonic acid, and not into urea and the corresponding acid. For the present, then, we cannot take this reaction into consideration.

The above brief summary of what work has been done on the constitution of the amides, shows clearly, 1st, that the question is in a very unsettled state; and 2nd, that what little evidence there is, points to a division of the amides into two groups, one containing oxamethane, the various carbamides, benzenesulfonamide; the other embracing acetamide, benzamide, and some of their substitution-products. The first group possessing the customary amide formula; the second having the imido hydroxy structure, and being the long-sought, ever-at-hand imido acids.

The present investigation unfortunately can bring almost nothing to the solution of the problem. The amides are characterized by a hopeless indifference to all the reactions that suggest themselves for study. But this very incapacity for reaction is in itself of interest, and in the importance attaching to the question, a brief outline of the work as planned and a short summary of the large number of experiments carried out, may find their excuse for publication.

The object in view was to find out if the classification arrived at above would stand closer scrutiny. For this purpose I subjected first the oxygen atom of the amides to a comparative examination, then the nitrogen atom, and finally the double linking that exists in the second group. In the first series the reagents employed were phosphorus trichloride, hydroxylamine, and alcoholic hydrochloric acid; in the second, nitrous acid and ethyl iodide; in the third, hydrocyanic acid and ethyl hypochlorite.

Summary of Experimental Work.

1. *Phosphorus Trichloride.*—Acetamide gives only a red,

sticky mass, containing chlorine, phosphorous acid, ammonia and acetamide. Hydrochloric acid is given off, but no acetonitrile or acetyl chloride whatsoever is formed.

Benzamide, warmed with the trichloride, gives 75 per cent. of benzonitrile. Ten grams of each were warmed on the water-bath for fifteen minutes, the mixture poured into water, extracted with ether, the ether-extract dried and fractioned. 6.1 grams benzonitrile were obtained, boiling between 187° and 189°; a trace of benzamide remained in the distilling flask.

Urethane is destroyed by excess of the trichloride; if less than one molecular equivalent be used, a portion of the urethane remains unchanged.

Oxamethane was boiled on the water-bath with excess of the trichloride for three hours, and suffered no change.

2. *Hydroxylamine.*—Urea and urethane have stood both with free hydroxylamine and its hydrochlorate for over two months, without showing any sign of reaction.

Methyl acetamide gives a color reaction with ferric chloride after standing several days with the hydrochlorate; but even after seven weeks the solution reduced Fehling's solution very strongly.

With diethylacetamide the same results were obtained, though in this case the experiments were varied by employing free hydroxylamine, and also a large excess of alkali. On boiling a solution of diethylacetamide and the hydrochlorate a constant evolution of gas takes place; after about about thirty hours the solution no longer reduces, but decomposition has gone on to such an extent that I have been unable to isolate the compound formed in sufficient quantity to determine whether it is ethenyl diethylamidoxime or ethenyl hydroxamic acid. However, diethylamine is to be found in the solution, and the reaction has therefore probably resulted in the formation of the latter substance.

Oxamethane has been shown to be attacked at the carbethoxyl group by free hydroxylamine.[1] On prolonged boiling with hydrochlorate the same result would appear to take

[1] Schiff and Monschli: Ann. Chem. (Liebig), **288**, 314.

place, for ammonium oxalate was obtained in considerable quantity.

3. *Alcoholic Hydrochloric Acid.*—This was an attempt to introduce ethyl into the possible hydroxyl group in acetamide and benzamide. After standing in the ice-chest for a month, a large amount of acetic and benzoic esters were obtained. There was no trace of the imido ethers.

4. *Nitrous Acid.*—This was employed in aqueous and in benzene solution, in the presence or absence of mineral acids. Scarcely any difference could be noticed in the behavior of benzamide, urethane, urea, and oxamethane, acetamide reacted markedly slower, but began to be attacked after ten minutes.

5. *Ethyl Iodide.*—The amides were heated with excess of this substance to 100°, for periods ranging from a day to a week. Formamide, acetamide and urea were decomposed after several days heating; urethane and oxamethane were decomposed much more slowly; in none of these cases was an addition-product obtained. Methylacetamide combines with ethyl iodide rapidly; the compound is very deliquescent and forms colorless needles. (Found, 55.3 per cent. iodine; calculated, 55.2 per cent.) Methylurethane was decomposed.

6. *Hydrocyanic Acid.*—Acetamide, acetanilide, benzaldiacetamide and benzamide were dissolved in anhydrous hydrocyanic acid, if necessary, with addition of ether or alcohol. After standing six days no sign of action could be perceived.

7. *Ethyl Hypochlorite.*—This reagent dissolves in an aqueous solution of acetamide, but the commencement of warm weather prevented any detailed investigation.

Conclusion.

There is only one result to be discussed, *viz.*, that obtained with phosphorus trichloride. It is quite impossible that in the above experiment benzamide passed into benzonitrile through the amide-chloride stage. If any intermediate product whatever was formed, it must have been the imide chloride. But the reaction may have simply been a splitting off of water. The proof that the latter explanation will not

hold is furnished by the indifference of oxamethane to the same reagent. Oxamethane loses water and passes into a nitrile just as readily as benzamide; and if the action of phosphorus trichloride is merely dehydrating, the reactions in both cases would have been identical. Now oxamethane has been shown to form an amide chloride, and this amide formula explains its indifference to the trichloride. Benzamide, on the other hand, reacts in the same manner with both chlorides, forms as first product not an amide, but an imide chloride, and therefore contains a hydroxyl group.

Wallach's theory of the action of phosphorus pentachloride on the amides is thus no longer universally applicable; though unfortunately there are at present no means of determining where its limits lie.

Further discussion at this point would be profitless. I would merely emphasize that the conclusions arrived at during the consideration of the literature are by no means final. Thus the action of hydroxylamine, be it as it may, is certainly not to be regarded as a direct metathesis, as is shown, *e. g.*, by the fact that with esters[1] it yields hydroxamic acid, and not alkylhydroxamic acids; the phenomena of addition play an important part in its reactions. The same may be true of the action of acetyl chloride, as has been suggested by Pictet.[2]

Mr. F. M. Tschirner carried out a large number of the experiments mentioned, and I should like to avail myself of this opportunity of thanking him for his earnest and valuable assistance.

CHROMIC HYDROXIDE IN PRECIPITATION.

By Harrison E. Patten.

The action of a number of metallic hydroxides in carrying down other substances in precipitation is well established. This "adhesion," as Ostwald calls it, is not limited to gelatinous precipitates, but is noted in the case of some crystalline precipitates, especially barium sulphate, which carries down iron, aluminum, etc., and is very hard to purify when once combined with them.

[1] Jeanrenand: Ber. d. chem. Ges., **22**, 1272.
[2] Ber. d. chem. Ges., **23**, 3011.

A. V. E. Young[1] has shown that the reaction between alum and potassium hydroxide is not to be represented by the usually accepted equation, but that the distribution of the constituents of the system about the line of solubility is a function of the temperature, volume and total mass of constituents. V. J. Hall has also shown in "A Study of Ferric Hydroxide in Precipitation," that ferric hydroxide under certain conditions decomposes potassium sulphate, carrying the sulphur trioxide into precipitation, leaving the potassium and thus manifesting true chemical action. A. Recoura[2] has shown that chromium forms complex acids, bases and salts, in which chromium, in combination with varying amounts of the radicle SO_4, acts as a complex radicle. The radicle SO_4 in these complex acids, bases and salts, gives no precipitate with barium chloride, and their existence is also proved by their heat of neutralization.

Working along the lines suggested above, I have investigated chromic hydroxide to ascertain the amount of disturbance under definite conditions; further, to answer, if possible, the question whether the chromium or the sulphuric acid, or the combined action of the two, causes this disturbance, and whether there is a recombination of the elements to form a new compound, or merely a mechanical action.

Solutions as described below were used in the work:

1. For the chromium solution 29.4815 grams pure potassium dichromate was reduced with strong hydrochloric acid, excess of acid driven off, and made up to one liter at 22°. This solution contained 0.02819 gram chlorine, and 0.01607 gram chromium sesquioxide per cc. It was unnecessary to determine the potassium.

2. A dilute solution of potassium hydroxide, standardized by titration against oxalic acid and gravimetrically. It contained 0.0350 gram potassium hydroxide per cc.

3. A dilute solution of sulphuric acid, standardized against the potassium hydroxide solution. It contained 0.04206 gram sulphuric acid per cc.

[1] A Thermochemical Analysis of the Reaction Between Alum and Potassium Hydrate. This JOURNAL, 8, 23.

[2] Recherches sur le Sulfate chromique, ses Transformations et les Acides complexes qui en derivent. Ann. chim. phys. [7], 4, (1895).

As a preliminary step, I determined the amount of potassium hydroxide required for exact precipitation of chromium in Solution 1. 24.86 cc. Solution 1 required 23.68 cc. potassium hydroxide for exact precipitation.

General Method.

The filtrates were analyzed and the percentage of each constituent found deducted from the percentage of the total introduced. The difference gives the percentage of the constituent in the precipitate, which may not be analyzed directly since washing, or diluting the solution in which the precipitate is formed, changes its composition.

The first point to determine is whether or not sulphur trioxide, chlorine, or potassium oxide is carried down by chromium when precipitated by six molecules of potassium hydroxide in the presence of four molecules of potassium sulphate, according to the equation :

$$Cr_2Cl_6 + 6KOH + 4K_2SO_4 = Cr_2(OH)_6 + 6KCl + 4K_2SO_4.$$

Blank Experiment.—First, a blank determination of the sulphur trioxide was made, the system being made up according to the above equation, leaving out the chromium chloride. 112.4 cc. potassium hydroxide and 46.5 cc. sulphuric acid, sufficient to form six molecules of potassium hydroxide and form four molecules of potassium sulphate were made up to 500 cc. at 22°, four portions were drawn off with a 50 cc. pipette and the sulphur trioxide determined as barium sulphate:

A. 0.1596 gram
B. 0.1602 gram } SO_3 blank for "total."

C. 0.1610 gram
D. 0.1604 gram } SO_3 blank for "filtrate."

Series I—Experiment F.

I took 112.4 cc. potassium hydroxide and 46.5 cc. sulphuric acid—sufficient to form six molecules of potassium hydroxide and four molecules of potassium sulphate—added 50 cc. chromium solution from the pipette and made up to 500 cc. at 22°. This I let stand about twenty minutes, shook well, and drew off four 50 cc. portions of precipitate and filtrate mixed, de-

Table—Series I.

Exp.	KOH.	Total Cr_2O_3.	Filtrate Cr_2O_3.	Precipitate Cr_2O_3.	Total SO_3.	Filtrate SO_3.	Precipitate SO_3.	Total K_2O.	Filtrate K_2O.	Precipitate K_2O.	Total Cl.	Filtrate Cl.	Precipitate Cl.	Percentage total. Cr_2O_3 in precipitate.	Percentage total. SO_3 in prec.	Percentage composition of precipitate. Cr_2O_3	Percentage composition of precipitate. SO_3.
A	50 cc. Cr_2Cl_6 3	.0804	.0732	.0072	.1596	.1610 / .1603 / .1606	.0000	.3031 / .3025 / .3028	.3047 / .3034 / .3040	.0000	.1447 / .1443 / .1445	.1437 / .1454 / .1445	.0000	8.99	0.00	100.00	0.00
B	3½	.0785	.0575	.0210	.1596	.1606 / .1595 / .1600	.0000	....	....	....	....	. .	....	26.75	0.00	100.00	0.00
C	4	.0808	.0507	.0301	.1593	.1594 / .1595 / .1594	.0000	.3266	.3270	.0000	.1425 / .1435 / .1430	.1432 / .1429 / .1430	.0000	37.59	0.00	100.00	0.00
D	4½	.0808	.0432	.0366	.1590 / .1593	.1592 / .1595 / .1593	.0000	....	....	....	....	....	...	45.70	0.00	100.00	0.00
E	5	.0803	.0255	.0548	.1592	.1531 / .1543 / .1537	**.0055**	.3543	.3553	.0000	.1423 / .1422 / .1422	.1427 / .1426 / .1426	.0000	68.47	3.45	90.84	9.16
F	6	.0800	.0000	.0800	.1565 / .1563	.1591 / .1602 / .1596	.0000	.3678 / .3675 / .3676	.3703 / .3700 / .3701	.0000	.1436 / .1418 / .1424	.1427 / .1426 / .1426	.0000	100.00	0.00	100.00	0.00
G	8	.0803	.0000	.0803	.1594	.1605	.0000	.4732	.4738	.0000	.1422 / .1420 / .1421	.1448 / .1448 / .1448	.0000	100.00	0.00	100.00	0.00
Blank	No Cr_2Cl_6	....	....	....	.1599 / .1602 / .1601	.1610 / .1604 / .1607	....	...	....	....	....	....	....	. .	....	....	....
Blank	50 cc. Cr_2Cl_6 No KOH	.0800 / .0800	....	....	....	....	....	....	....	....	.1416 / .1418 / .1417	....	....	....	....	...	....

livered each portion in a clean, dry beaker and set aside to be analyzed as "totals" for potassium oxide, chlorine, sulphur trioxide and chromium sesquioxide. The remainder of the precipitate and solution were thrown upon a dry filter, the filtrate brought back to 22° and five 50 cc. portions drawn off with the pipette and analyzed as "filtrates" for potassium oxide, chlorine, sulphur trioxide and chromium sesquioxide. Not a trace of chromium was found in the filtrate.

The "totals" were redissolved by hydrochloric acid, reprecipitated by ammonium hydroxide, boiled, and the precipitate washed till no trace of sulphur trioxide could be detected by the barium chloride test. The filtrate and washings were then evaporated to convenient bulk and the sulphur trioxide determined as barium sulphate.

In determining potassium oxide the method is the same as for sulphur trioxide, save that the precipitate of chromium hydroxide is washed till no residue is obtained by evaporating the washings on platinum foil. The washings are then evaporated to dryness, the ammonium salts volatilized, the residue extracted with water, filtered and evaporated, and ignited in a platinum dish as potassium sulphate. The chlorine is determined in the presence of chromium, the totals being redissolved by nitric acid and the chlorine precipitated and weighed as silver chloride. A wash-water containing 25 cc. strong nitric acid and 0.1 gram silver nitrate per liter is found adequate to remove all chromium from the silver chloride.

The "filtrates" were analyzed in the same manner as the "totals." It was assumed that re-solution with hydrochloric acid and reprecipitation by ammonium hydroxide liberates any constituents carried down in the precipitation with potassium hydroxide. This assumption was shown to be correct by comparison of the blank experiment with the totals, and by the constancy of the totals in different experiments.

If, now, the same quantities of sulphur trioxide, chlorine and potassium oxide are found in "totals" and "filtrates," the equation

$$Cr_2Cl_6 + 6KOH + 4K_2SO_4 = Cr_2(OH)_6 + 6KCl + 4K_2SO_4$$

completely represents the reaction. In Series I, Section F, the results confirm this equation.

Experiments E, D, C, B, A, and G were made, using, respectively five, four and one-half, four, three and one-half, three, and eight molecules of potassium hydroxide to precipitate the chromium. Each experiment was made with the same quantity of chromium chloride and potassium sulphate present as in Experiment F, the method of analysis being the same throughout. Throughout this series adhesion is only noted once, in Experiment E, where five molecules of potassium hydroxide were used, 3.4 per cent. of the total sulphur trioxide introduced is carried into precipitation, the potassium oxide and chlorine remaining undisturbed. (See Section E, Series I.)

Series II.

A series of experiments under the same conditions as Series I, but with no sulphate present, was attempted; the object being to ascertain if chlorine or potassium oxide was disturbed in absence of sulphate.

A system containing three molecules of potassium hydroxide to one of chromium chloride was made up, and on standing three hours the precipitate first formed completely redissolved, showing that time is a factor in the action.

Another system identical with the above was then made up, "totals" drawn off as quickly as possible, and the remaining solution and precipitate thrown upon a dry filter. But the precipitate could not be filtered out by the closest quantitative filter-paper. Further, the "totals" did not settle clear, but redissolved on standing.

A system containing four molecules of potassium hydroxide to one of chromium chloride was made up. The precipitate first formed would not settle, could not be filtered and redissolved completely in four hours. This clear solution was then brought to $-1\frac{1}{2}°$, but no precipitate separated.

A system containing five molecules of potassium hydroxide to one of chromium chloride was made up. The precipitate formed would not settle, could not be filtered and redissolved completely in twelve hours. This clear solution was boiled,

but gave no precipitate; it was cooled to —1°, but no precipitate separated.

A system containing six molecules of potassium hydroxide to one of chromium chloride was made up. It gave a definite precipitate; the results are:

Cl in "total"	0.1432	Cr_2O_3 in "total"	0.0802
Cl in "filtrate"	0.1430	Cr_2O_3 in "filtrate"	0.0000
Cl in "precipitate"	0.0002	Cr_2O_3 in "precipitate"	0.0802

showing no chlorine carried down.

Throughout Series I, with potassium sulphate present, the fractional precipitations gave definite precipitates, filtering clear and settling clear. In contrast to this, note the resolution and failure to filter and settle of the precipitates formed in absence of sulphate in Series II. Further, the "totals" and "filtrates" of all the experiments of Series I had to stand from three to six days before they were examined. In no case did the "totals" redissolve, but on the contrary, in one or two instances, the "filtrates" gave more precipitate.

To make sure that this precipitation in presence of sulphate was due to the sulphate, I added magnesium sulphate to a redissolved system containing five molecules of potassium hydroxide to one of chromium chloride. The precipitation was immediate and almost complete; the precipitate was then redissolved on the filter with dilute hydrochloric acid and tested for magnesium with the aid of sodium phosphate. Not the slightest trace was shown. Calcium, sodium, and ammonium sulphates were respectively added to the redissolved system, and in every case precipitation was instantaneous and nearly complete. Chlorides and nitrates do not precipitate chromium from this solution.[1]

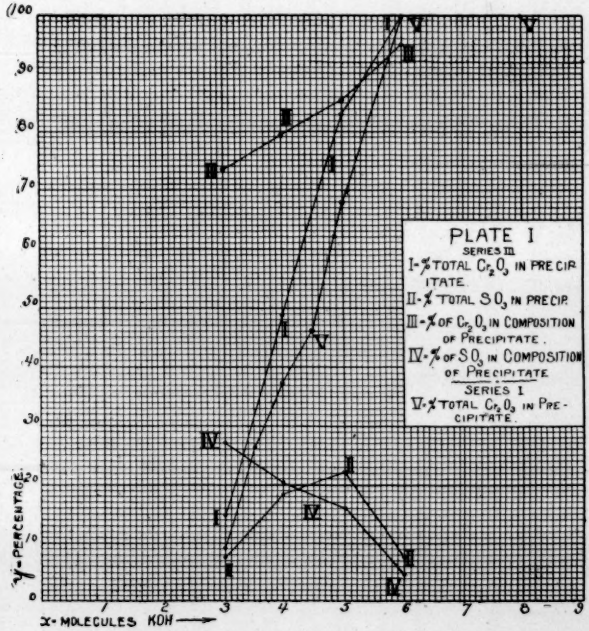
Series III.

To investigate this action further, the amount of chromium chloride and potassium hydroxide was tripled, but the sulphate left the same as in Series I. Experiments were made with three, four, five, and six molecules of potassium

[1] Potassium chloride, magnesium chloride, potassium nitrate and barium nitrate were used.

hydroxide present, the method of analysis being the same as in Series I. (For results see Sections N, O, P, Q, Series III, in table, also Plate I.)

Reliabitity of Results.—The differences upon which my conclusions are based are not great, varying from 3.4 to 22.1 per cent. of the total quantity of sulphur trioxide introduced. But



since the difference between duplicate "totals" and "filtrates" in no case exceeds 1 per cent. of the total quantity measured, and in most cases is below 0.5 per cent., their significance cannot be questioned.

Discussion.—Series I shows sulphur trioxide carried down only at five molecules, and then only 3.45 per cent. of the

Table—Series III.

Exp.	KOH.	Total Cr_2O_3.	Filtrate Cr_2O_3.	Precipitate Cr_2O_3.	Total SO_3.	Filtrate SO_3.	Precipitate SO_3.	Total K_2O.	Filtrate K_2O.	Precipitate K_2O.	Total Cl.	Filtrate Cl.	Precipitate Cl.	Percentage total. Cr_2O_3 in precipitate.	Percentage total. SO_3 in precipitate.	Percentage composition of precipitate. Cr_2O_3.	Percentage composition of precipitate. SO_3.
N	3(50 cc. Cr_2Cl_6) (3)$_2$	.2349	.2016	.0333	.1616	.1495 / .1490 } .1493	.0123	....	....	....	.4276	.4279 / .4293 } .4286	.0000	14.18	7.61	73.01	26.99
O	(4)$_2$	.2357	.1202	.1155	.1617	.1320 / .1321 } .1321	.0 29	....	....	....	....	....	....	49.00	18.30	79.60	20.40
P	(5)$_2$	.2350	.0396	.1954	.1619	.1262 / .1258 } .1260	.0359	.6730	.6743	.0000	.4302	.4281	.0021	83.15	22.17	84.48	15.52
Q	(6)$_2$	.2353	.0000	.2353	.1615	.1494 / .1502 } .1498	.0117	.7466	.7455	.0011	....	....	....	100.00	7.24	95.27	4.73
R	Blank	....	....	....	.1601	....	....	....	...	....	....	....	....	....	....	...	....
S	50 cc. Cr_2Cl_6 Blank	....	....	....	....	....	....	....	....	....	{ .1426 / .1433 } .1430 × 3 } = .4290	....	....	...	....	....	....

total quantity. It was considered doubtful if much reliance should be placed on such slight evidence. But the results of Series II showed conclusively that the sulphate entered into the reaction, since no precipitation takes place at two, three, four or five molecules of potassium hydroxide in absence of potassium sulphate. The qualitative work, varying the base in combination as sulphate, shows that this effect is due to the sulphur trioxide and not to the base.

These facts may be taken as an answer to the first question, "Whether the chromium, or sulphuric acid, or the combined action of the two, causes this disturbance." They show conclusively that the action between the chromium sesquioxide and sulphur trioxide is mutual.

The results of Series III show still more conclusively that there is a recombination of the elements to form a new compound. If this "adhesion" were indeed mechanical in its nature, we should find the action proportional to the amount of precipitate present. But Plate I, Curve II, shows practically the same quantity of sulphur trioxide carried down at three molecules as at six, while there is approximately seven times as much precipitate present at six as at three. Also, at five molecules there is over three times as much sulphur trioxide carried down as at six molecules, and at four molecules a trifle less than at five molecules. The action then is truly chemical in its nature.

Considering Series I, II and III, we see that this disturbance affects only the sulphur trioxide, the chlorine and potassium remaining in solution. The sulphur trioxide then must be united directly to the chromium, or possibly a complex compound is formed.

From these considerations it is beyond question that the sulphur trioxide enters into the reaction at three, three and one-half, four, four and one-half, and possibly at six molecules of potassium hydroxide, as well as at five molecules in Series I. (See table.) But the analyses do not show sulphur trioxide carried down at these points. In explanation of this, I conceive that there is a primary and a secondary action here. First the formation of the new combination of sulphur trioxide and chromium sesquioxide, then a splitting

up of the compound by water. The power of water to break up these compounds composed of aluminum sesquioxide and sulphur trioxide, iron sesquioxide and sulphur trioxide, and chromium sesquioxide and sulphur trioxide is well recognized, and it was to overcome the obstacle which this fact presents, that the method of differences has been used throughout this work. The chromium sesquioxide having been thus precipitated by agency of the sulphur trioxide, it appears to remain in precipitation.

Having thus considered the disturbance at complete and fractional precipitation, I purpose at a later date to investigate the action at fractional re-solution of chromium hydroxide by excess of potassium hydroxide.

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AN EMPIRICAL RELATION BETWEEN MELTING-POINT AND CRITICAL TEMPERATURE.

BY F. W. CLARKE.

Although many papers have been written upon relations between boiling-point and critical temperature, the melting-points of substances, at least in this connection, seem to have been little considered. And yet a glance at the subject will indicate its importance. For any substance the limits of the solid state are the absolute zero and the melting-point; while the extreme limits of the liquid condition are the melting-point and the critical temperature. A comparison of these values, therefore, will give for each substance the relative thermometric lengths of the two states of matter, and the results obtained, although empirical, have very decided interest. Unfortunately many of the compounds of which the critical temperature is known, have never had their melting-points determined, and hence the available data are very meagre.

Representing the ordinary melting-points by t and the critical temperatures by T, the relation between them, on the absolute scale, is best represented by the formula

$$\frac{T+273}{t+273}.$$

For the following substances this ratio is very nearly $= 2$,

the data, except when otherwise stated, being taken from Landolt and Börnstein's tables. Fractions of degrees less than 0.5 are neglected.

	t. Degrees.	*T.* Degrees.	*Ratio.*
Nitrogen,	—214.0	—146.0	2.18
Carbonic oxide,	—207.0	—139.5	2.02
Argon,[1]	—190.0	—121.0	1.83
Methane,[1]	—186.0	— 82.0	2.19
Hydrochloric acid,	—112.5	+ 52.0	2.02
Hydrogen sulphide,	— 86.0	+100.0	2.00
Ammonia,	— 75.0	+130.0	2.03
Benzene,	+ 3.0	+288.5	2.04
Acetic acid,	+ 17.5	+322.0	2.05

In other words, for these nine substances the absolute melting-point is very nearly, if not exactly, one half the absolute critical temperature, and the thermometric lengths of the solid and liquid states are approximately equal. Assuming the errors of observation to be evenly distributed in each case between the two temperature factors, we may average the latter and so compare the mean values with those actually recorded. The results are as follows:

	FOUND.		AVERAGE.	
	t. Degrees.	*T.* Degrees.	*t.* Degrees.	*T.* Degrees.
N_2,	—214.0	—146.0	—211.0	—149.0
CO,	—207.0	—139.5	—206.5	—140.0
A,	—190.0	—221.0	—195.0	—117.0
CH_4,	—186.0	— 82.0	—180.0	— 87.0
HCl,	—112.5	+ 52.0	—111.0	+ 51.0
H_2S,	— 86.0	+100.0	— 85.5	+100.5
NH_3,	— 75.0	+130.0	— 73.0	+128.0
C_6H_6,	+ 3.0	+288.5	+ 4.0	+287.0
$C_2H_4O_2$,	+ 17.5	+322.0	+ 22.0	+317.9

When we consider the uncertainty of some of the measurements, the agreement is certainly very close.

This simple relation, however, is not general. In all I have examined the data for about thirty substances, and no universal rule appears. There are, nevertheless, other regularities apparent which connect certain allied substances with one another, and two such groups I subjoin:

[1] Olszewski.

	t. Degrees.	*T.* Degrees.	Ratio.
C_2N_2,	— 34.5	+124.0	1.67
N_2O_4,	— 10.0	+171.0	1.64
NO,	—167.0	— 93.5	1.70
N_2O,	— 99.0	+ 35.5	1.77

These compounds run closely together and are alike in being gaseous compounds of nitrogen. The next group contains five aromatic bodies.

	t. Degrees.	*T.* Degrees.	Ratio.
o-Xylene,	—45.0[1]	+358.0[3]	2.77
m-Xylene,	—53.0	+346.0[3]	2.81
C_6H_5Cl,	—40.0	+361.0	2.78
C_6H_5Br,	—30.5[1]	+397.0[3]	2.75
C_6H_5I,	—28.5[1]	+448.0[3]	2.94

Here again there is an essential identity of ratio with related constitution, a fact which suggests that the method of discussion applied to larger masses of data, is likely to give information of considerable theoretical value.

For most of the other substances which I have considered, the ratio ranges between 2.2 and 3.0. For carbon dioxide its value is only 1.41, for ether it is 3.06. In the latter case the thermometric lengths of the solid and liquid states, therefore, are as one to two. A few bodies only give ratios higher than three. These are—besides ether—

CS_2,	3.36
PCl_3,	3.47
Alcohol,	3.59

Other values are :

Br_2,	2.17	H_2O,	2.34
Cl_2	2.44	$SNCl_4$,	2.47
SO_2,	2.22	$CHCl_3$,	2.62
CCl_4,	2.25	C_2H_4,	2.75

Paraxylene gives the ratio 2.14, varying widely from its isomers.

Concerning the quantity of heat necessary to raise a body from absolute zero to the melting-point, and then from the

[1] v. Schneider. [2] Altschul.
[3] Young : Theoretically determined.

melting-point to the critical temperature, the data are altogether wanting; but the ratio between those two quantities would certainly be significant. For the regularities which I have here pointed out I have no theoretical explanation to offer. If, however, they serve to stimulate the determination of other low temperature melting-points for compounds of which the critical temperatures are known, this paper will have served a useful purpose. The relations which are already apparent cannot be meaningless, and others must be discoverable.

ALUMINUM ALCOHOLATES.

By H. W. Hillyer.

In work preparatory to using the method of Wislicenus and Kaufmann[1] for reduction in neutral solutions by use of amalgamated aluminum, observations were made which have led to the work of which this is a preliminary notice.

According to these authors amalgamated aluminum does not act on absolute alcohol, but can be preserved for use covered by absolute alcohol. By following their directions, we obtained an amalgam having properties like those described; but in order to avoid all contact with the air and the degeneration of the amalgam, caused by its coating over with hydroxide, instead of an aqueous solution of mercuric chloride, a solution of mercuric chloride in absolute alcohol was used. When this was brought in contact with chipped aluminum an evolution of gas soon commenced, and instead of ceasing, as might have been expected, when the little water in the alcohol had been decomposed, it increased in rapidity and the alcohol became heated nearly or quite to the boiling-point.

The action gradually became more moderate, but continued so long that on cooling the whole gelatinized. The most probable reaction is $Al + 3C_2H_6O = Al(OC_2H_5)_3 + 3H$.

Knowing from the work of Gladstone and Tribe that aluminum alcoholates, in contrast to all other known alcoholates, can be distilled under diminished pressure, an attempt was made to distill the product obtained. After the

[1] Ber. d. chem. Ges., 28, 1323.

alcohol, a gray distillate of mercury came over under 20 mm. pressure, and then white fumes and an oily liquid solidifying in the receiver. The distillate contains much aluminum, but is greatly contaminated with mercury.

In the attempt to avoid the presence of mercury, which made the purification difficult, other salts soluble in alcohol were tried, but with no special result until, on using fuming stannic chloride, a reaction took place similar to that with the mercuric chloride. In this case spongy tin separated, a gas was rapidly evolved, and the liquid became quite hot. In both cases an application of external heat starts a new evolution of gas. When no more gas was evolved the alcohol was distilled off and the residue in the retort subjected to distillation under diminished pressure. A distillate was obtained rich in aluminum and containing no tin. Determinations of the amount of aluminum seemed to indicate that the substance might be aluminum hydroxydiethylate, $Al(OC_2H_5)_2OH$, but work on the action of ethyl alcohol was temporarily interrupted at this point. Two experiments with methyl alcohol gave good evolution of gas, but no substance could be distilled under a diminished pressure. The retort after distilling off the alcohol contained apparently nothing but aluminum oxide or hydroxide. Work with normal propyl alcohol has resulted in showing definitely that aluminum tripropylate is formed under similar conditions. An account of this work will soon be published in detail.

Isopropyl and amyl alcohol also react on aluminum in the presence of aluminum chloride and the spongy tin formed by its action on stannic chloride in solution in these alcohols. The aluminum is dissolved to give a solution from which it is precipitated, probably as hydroxide, on addition of water or by mere action of the moisture of the air.

The writer desires to reserve for the present the privilege of investigating the action of aluminum on alcohols to which mercuric chloride and stannic chloride have been added, and to investigate the action of sulphur dioxide and of hydrogen sulphide on the alcoholates thus formed.

ORGANIC CHEMICAL LABORATORY,
UNIVERSITY OF WISCONSIN.
May 29, 1896.

THE CONDUCTIVITY OF SOLUTIONS OF ACETYLENE IN WATER.

By Harry C. Jones.

The comparatively high conductivity of water solutions of acetylene, found by Mr. Allen and myself,[1] has always been more or less unintelligible to us, and has led me, in the absence of Mr. Allen, to repeat the work. The results obtained showed acetylene to be very considerably dissociated in water, yet these solutions did not show an acid reaction with litmus. The gas used in the first work was prepared from cuprous acetylide furnished us by Prof. Keiser, being liberated from the compound by warming with a solution of potassium cyanide, as he directed. The acetylene solutions were tested for all the impurities which we thought could possibly be formed in the reaction, and found to be free from them all, as far as could be determined by chemical methods.

It occurred to me later that in the reaction between potassium cyanide and cuprous acetylide, a small quantity of ammonia might be generated by the action of the potassium hydroxide formed during the reaction on the excess of potassium cyanide. To test this point, it was decided to prepare cuprous acetylide perfectly free from ammonia, to liberate the acetylene by means of hydrochloric acid, and then to determine whether the acetylene thus prepared had the same conductivity as that obtained by the method suggested by Keiser. The results of this work showed that the acetylene prepared as described above and carefully washed to remove all traces of hodrochloric acid, had very slight, if any conducting power. As we stated in our first paper, the error in standardizing the solutions is necessarily large, but taking this into account, I was never able to obtain a solution of acetylene prepared by the action of hydrochloric acid on the acetylide, which had a molecular conductivity greater than unity.

Some very carefully washed cuprous acetylide was then treated with a solution of potassium cyanide, exactly as in the earlier work, to determine whether ammonia was liberated in the reaction in quantities sufficient to be detected by chemical

[1] This Journal, 18, 375.

means. The reagents, which were applicable under the conditions, failed to show the presence of ammonia. To my surprise, the acetylene solutions thus obtained, conducted to about the same extent as those prepared from the acetylide by means of hydrochloric acid.

This fact, together with the results first obtained, can, so far as I can see, be explained in only one way; that the acetylide from which the acetylene first studied was obtained, must have contained a small amount of some volatile impurity, probably ammonia, whose presence was not suspected by us, and which therefore escaped detection.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY.
MAY, 1896.

WATER SUPPLY. (CONSIDERED PRINCIPALLY FROM A SANITARY STANDPOINT). By WILLIAM P. MASON, Professor of Chemistry, Rensselaer Polytechnic Institute. John Wiley & Sons: New York. Chapman & Hall: London. 1896.

Within a moderate compass Professor Mason has brought together for readers of English a large amount of valuable information in regard to water as used by man for drinking and other domestic purposes.

The form in which this information is presented is likely to make the book useful to the general public, as well as to those whose duties more particularly call for knowledge in regard to the important question of water supply for large or considerable populations.

So extensive and important is this question, however, that perhaps no two writers would agree exactly as to the scope to be given a work of the kind under review, or the precise division and order of presentation of the subject.

The chapter devoted to a discussion of the relation of polluted drinking water to disease is calculated to impress the reader with the strength of the evidence in regard to this relation. One point perhaps it would have been well to explain a little more fully. It is said, on p. 96: "No weight should be attached to the argument, so often advanced by the individual householder, that he and his family 'have used the water without evil result for fifty years.' A single family is too small a collection of units upon which to base any estimate touching the question at issue." It ought to be made clear to any one using such an argument, the force of which not unnaturally appears to the average mind very great, that a well so situated as to admit of organic polluting material reaching it may *actually* yield water which produces no disease for fifty years, and yet suddenly become most dangerous from the presence in its immediate neighborhood of a single case of typhoid fever, imported perhaps from a distance.

The purification of water by filtration on the large scale, whether in filter beds of great area through which the water passes by gravity only, or in filtering cylinders under pressure and with previous addition of alum, seems likely to prove a matter of increasing importance in the future in this country, and is treated of in a separate chapter, with illustrative engravings. In connection with the question of natural purification of water the dangerous error is pointed out of the common impression that in frozen form polluted water may be trusted to be wholesome.

In regard to the *avoidance* of pollution in water to be col-

lected for human use, the remarks as to the proper care of a water-shed after it has been selected deserve to be carefully considered and acted upon. They might probably have been exhibited with advantage somewhat more in detail.

The chapter on stored water gives useful facts bearing on the construction and maintainance of reservoirs, but questions of this kind are usually complicated in the most serious way with engineering and financial considerations, so that nearly every case needs practically to be dealt with as a special one.

There are some very judicious cautions as to the limitations within which water supply can be counted on from driven wells or from deep bored, so-called artesian wells, for the advantages of which, real to a certain extent, extravagant claims are not unfrequently made.

The methods for the chemical examination of natural waters are treated in a fairly balanced and impartial way, and the all important question of the interpretation to be put upon the results of such an examination is dealt with in a like spirit of undogmatic common sense. The same remark may be made in respect to the discussion of the bacteriological examination of water, the attempt being made to show in what special directions this mode of investigation is most likely to be of real use, without giving it undue and exaggerated importance.

In regard to the quantity of water needed *per capita* by a given population, one might wish for fuller discussion of the possible means of preventing such enormous waste as occurs in almost all cities and towns, and the special topics of "hardness," with its relations to health, soap consumption, interference with steam boiler use, &c., of the action of water upon lead and other metals, and of the particular relations of the foreign substances in natural waters to industrial use by brewers, dyers, paper makers, etc., are treated only in a very condensed way.

On the whole the book must be pronounced a useful and valuable addition to technological literature. J. W. M.

A Dictionary of Chemical Solubilities, Inorganic. By Arthur Messinger Comey, Ph.D., formerly Professor of Chemistry, Tufts College. Macmillan & Co.: London and New York. 1896.

This book is likely to be looked upon with mixed feelings by those who most need the information it compiles. It certainly represents much labor, and labor which cannot be said to have been altogether thrown away. Professor Storer's book on the same general plan, published in 1864, has long been out of print, and in this new volume it has been proposed to include much new matter which has accumulated within

the last thirty years, and to omit some of the older statements which have undergone correction and are not worth reproduction on merely historical grounds. Yet the result of the compiler's work is not altogether satisfactory.

As a matter of practical convenience the carrying into a work of this kind the distinction between organic and inorganic substances is not desirable, only the latter being included. The preface does not hold out the expectation of another volume, to include organic substances. Storer's book contained both. For an analytical chemist it is awkward to find no mention of such familiar salts as sodium acetate and ammonium oxalate. For practical purposes it is perhaps well to include, as did Storer, not only cases of simple solution, in the ordinary sense of the term, but also those of solutions resulting from evident chemical change. Yet the statement in regard to mercuric oxide—"Sol. in KI+Aq."—does not read well; the same remark applies to the assertion that sulphur trioxide is "miscible with water"; one does not see why silver should be recorded as—"Sol. in hot conc. H_2SO_4 with evolution of SO_3"—while no similar statement is made as to mercury; and if such cases are to be included at all it would seem to be quite proper to give the "solubility" of chlorine in carbon disulphide, since the products of interaction, carbon tetrachloride and sulphur monochloride, are both liquid at ordinary temperature and pressure.

Accuracy is of course the feature most of all to be desired in a work of this kind. The author expresses in the preface his doubt that errors have been entirely avoided. Without any very extensive collation with original authorities, the comparison of a considerable number of individual statements gives a very good general impression of the care with which the work has been prepared. Here and there some small errors are noticeable. On p. 204 the name Carnelley is given as Cornelley, and on p. 161 the writer of this notice happened to notice his own name given as authority for the solubility in dilute NH_4Cl + Aq. of *potassium* fluosilicate instead of *barium* fluosilicate (as correctly quoted on p. 160).

Some of the older ways of looking at chemical facts are reflected in statements like that on p. 3, quoted from Frémy, as to potassium aluminate—"Decomp. by dissolving in pure H_2O with separation of Al_2O_3." Objection may well be made to some of the forms of expression, such as on p. 148—"Didymium, Di, slowly decomp. by H_2O,"—or, on p. 316—"Phosphorus, P_4. (a) Ordinary phosphorus. Insol. in H_2O, but slowly decomp. thereby,"—or, on p. 196—"Iron carbonyl. Slowly decomp. on air,"—or on p. 269—"Nitrogen sulpho-

chloride. Unstable on air." And it is not easy to see the advantage of including the names of a number of substances in regard to which no statement whatever is made, or only some statement without bearing on solubility. Examples are afforded by such entries as the following—"Ammonium nickel cyanide, $2NH_4CN$, $Ni(CN)_2$. Easily decomposed." "Barium dithionate chloride, BaS_2O_4, $BaCl_2 + 4H_2O$. (Fock and Klüss, B. **23**, 3001.)" "Potassium fluoxypercolumbate, $2KF, CbO_2F_3 + H_2O$. (Piccini, Z. anorg. **1**, 51.)" "Platinum antimonide, $PtSb_2$. (Christofle, 1863.)" "Terbium, Tr. Metal has not been isolated. Has been decomp. into two or more elements by Krüss (Z. anorg. 4–27.)"

Some of the collections of modern data on particular points are valuable, as for instance those in regard to the attackability of various kinds of glass by water and watery solutions, and those on the relations of the saline and other constituents of natural waters to their action upon metallic lead. The book is neatly printed, and there is at the end a useful table of the principal scientific periodicals referred to, enabling the date of a reference to be found from the series and volume or *vice versâ*. J. W. M.

MILK, ITS NATURE AND COMPOSITION. A HAND-BOOK ON THE CHEMISTRY AND BACTERIOLOGY OF MILK, BUTTER AND CHEESE. By C. M. AIKMAN, M.A., D.Sc. Adam and Charles Black. London.

The aim of the book is to present in a brief and popular way the more important facts of the chemistry and bacteriology of milk and its products. The work is admirably adapted to the needs of intelligent dairymen, and will be found instructive by all non-professionals who wish to understand in a general way the important matters of which it treats.